

July, 1931

RUBBER CHEMISTRY AND TECHNOLOGY

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RUBBER DIVISION of the AMERICAN CHEMICAL SOCIETY



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RUBBER CHEMISTRY AND TECHNOLOGY

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Editor.....C. C. DAVIS
Associate Editor.....H. L. FISHER
Secretary-Treasurer.....H. E. SIMMONS

Vol. IV

July, 1931

No. 3

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RUBBER CHEMISTRY AND TECHNOLOGY

RUBBER CHEMISTRY AND TECHNOLOGY is published quarterly under the supervision of the editors representing the Rubber Division of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

RUBBER CHEMISTRY AND TECHNOLOGY may be obtained in one of three ways:

(1) Any member of the American Chemical Society may become a member of the Rubber Division upon payment of the dues (\$2.00) to the Division and thus receive RUBBER CHEMISTRY AND TECHNOLOGY.

(2) Any one who is not a member of the American Chemical Society may become an Associate Member of the Rubber Division (and also a member of his local group if desired) upon payment of \$4.00 per year to the Treasurer of the Rubber Division, and thus receive RUBBER CHEMISTRY AND TECHNOLOGY.

(3) Companies and Libraries may subscribe to RUBBER CHEMISTRY AND TECHNOLOGY at a subscription price of \$6.00 per year.

All applications for regular or for associate membership in the Rubber Division with its privilege of receiving this publication, all correspondence about subscriptions, back numbers, changes of address, and missing numbers and all other information or questions should be directed to the Secretary-Treasurer of the Rubber Division, Professor H. E. Simmons, Easton, Pennsylvania, or University of Akron, Akron, Ohio.

Rubber Division Activities

H. E. SIMMONS, Secretary-Treasurer of the Rubber Division of the American Chemical Society

The Rubber Division of the American Chemical Society

Officers

Chairman.....H. A. WINKELMANN, Palmer Carbon Company
Vice-Chairman.....E. R. BRIDGWATER, E. I. du Pont de Nemours & Co.
Secretary-Treasurer.....H. E. SIMMONS, University of Akron, Akron, Ohio
Executive Committee. STANLEY KRALL, G. K. HINSHAW, N. G. MADGE, D. J. BEAVER, H. F. PALMER
Sergeant-at-Arms.....E. NAHM

General Meeting in April, 1931

The Spring meeting of the Rubber Division was held on April 1 and 2, 1931, in the Severin Hotel, Indianapolis. The following program was presented:

Wednesday, April 1, 1931

- 9:30 A.M. K. J. Soule. The Effect on Vulcanized Rubber Compounds of Immersion in Boiler Water.
9:55 A.M. W. B. Wiegand and J. W. Snyder. Some Properties of Carbon Black. I—Adsorption.
10:15 A.M. E. O. Dietrich and J. M. Davies. Scorching and Other Plasticity Changes in Rubber Compounds on Heating.
10:40 A.M. M. J. DeFrance and W. J. Krantz. The Value of Softeners in Tread Stock.
11:00 A.M. Recess. Sale of Banquet Tickets.
11:10 A.M. R. P. Dinsmore. Report of Physical Testing Committee.
11:20 A.M. H. L. Trumbull. Report of Papers Committee.
11:30 A.M. H. W. Greenup. Effect of Various Factors upon the Rate of Deposition of Latex on Porous Molds.
11:50 A.M. Adjourn.

Thursday, April 2, 1931

- 9:30 A.M. Thomas Midgley, Jr., Albert L. Henne, and Mary W. Renoll. Natural and Synthetic Rubber. VIII—The Solubility Fractionation of Natural Rubber.
9:50 A.M. V. N. Morris. Permeability of Rubber to Air. II—Effect of Stretch, Thickness, Milling, Compounding Ingredients, Kind of Crude Rubber, and Temperature of Vulcanization.
10:15 A.M. C. W. Sanderson. Value of Rubber Hydrocarbon in Reclaimed Rubber.
10:35 A.M. Charles W. Stillwell and George L. Clark. An X-Ray Diffraction Study of Chicle.
10:55 A.M. Charles W. Stillwell and George L. Clark. Further X-Ray Studies of Gutta-Percha and Balata.
11:15 A.M. S. D. Gehman and J. S. Ward. A Micro-Turbidimeter for the Determination of the Rubber Content of Latex.

11:35 A.M. Henry F. Palmer, George W. Miller, and John E. Brothers. The Effect of Scrap Drying Temperature upon Reclaimed Rubber Quality.

11:55 A.M. Business Meeting.

12:00 NOON Adjourn.

At the business meeting of the Division the report of the *Physical Testing Committee* was presented by R. P. Dinsmore, and by motion was accepted. Following is the report:

"In organizing the Physical Testing Committee last fall there was some doubt as to the nature of the work with which the Committee might properly occupy itself during the year. The somewhat diverse opinions of the Executive Committee were taken into consideration, together with the experience of the former Physical Testing Committees of the past few years.

"The first meeting of the Committee was held October 23, 1930, in the offices of the R. T. Vanderbilt Co., New York City. There were present Messrs. Carpenter, Cooper, Dinsmore, and Morgan. At this meeting it was agreed that the most suitable activity would be the collection of data on the operating conditions for various physical tests other than tensile tests, with the idea of informing the Rubber Division as to the present operating limits and, if possible, to suggest standards. A number of different tests were considered, but it was finally decided to deal first with bomb and oven aging, and artificial light tests.

"The Akron members of the Committee agreed to hold a sub-committee meeting for the purpose of outlining a tentative questionnaire, to be submitted to the entire Committee for revision and approval. Such a meeting was held at the Akron University Club, Feb. 9, at which time questionnaires were outlined and some discussion was held regarding the laboratories to which questionnaires would be directed. These questionnaires have been submitted to the other members of the Committee, and comments have been received from most of the members. We expect to circularize the industry shortly with the revised questionnaires, after which the necessary work of tabulating the data will be undertaken.

"The Committee now consists of Messrs. Ackerman, Busenburg, Carpenter, Cooper, Morgan, Schatzel, and the Chairman. We believe that this is sufficiently representative of the various phases of the rubber business, so an intelligent analysis of the data from the questionnaires may be made."

H. L. Trumbull, as Chairman of the Papers Committee, made the following report, which upon motion was accepted.

"The Papers Committee recommends as follows:

"1. The time required for presentation of each paper, including discussion, shall be assigned by the Secretary of the Division. A minimum of ten minutes for the discussion is suggested.

"2. The chairman of the meeting will provide an alarm clock, which will be set for the allotted time and will give a two-minute warning signal.

"3. The scheduling of papers at a definite time is recommended, and will necessitate rigid adherence to the order in which papers are presented. This will permit all members of the American Chemical Society to attend our meetings in order to hear specific papers without uncertainty or undue delay.

"4. The committee reviewed and decided to adhere to the six weeks' rule.

"5. It is agreed that when a paper has been adversely reported for presentation by two reviewers it will be submitted to two additional reviewers. The Secretary after receiving the comments of the four reviewers has discretionary power, and can, if the author persists in his desire, schedule the paper for presentation, exercising

the prerogative granted to the secretary in paragraph 1, of limiting the time of presentation.

"Publication of papers rejected by four reviewers is a possibility so remote as to require no comment.

"6. The authors of papers are requested to use the chemical names in preference to the trade names of materials mentioned. If trade names or designations are employed, it is desirable at least once in the paper to define the chemical composition of the material in question."

The report of the Secretary showed at the time of the meeting the Division had 387 members, 110 associate members, 69 subscribers, and 30 Honorary Members, a total of 596 members, 48 members, 22 associate members, and 17 subscribers were dropped during the past year.

The Following Resolutions were presented by *Resolution Committee*, and by vote approved by the Division.

1. *Resolved*, The Rubber Committee expresses its cordial thanks to the Indiana Section and the local committee, whose efforts have contributed to the success of the meeting and the pleasure of the members.

2. *Resolved*, that the thanks of the Rubber Division also be extended to the Banquet Committee, S. L. Weller, J. E. Cady, and E. R. Waite, to whom credit is due for the enjoyable dinner and entertainment on Wednesday evening.

C. R. BOGGS
C. W. SANDERSON
A. H. FLOWER,
Resolution Committee

It was moved and carried that at the future meetings no Resolution Committee be appointed unless something special required the preparation of suitable Resolutions.

The Division had in general attendance 150 at both sessions.

The Rubber Division dinner was held Wednesday night at the Columbia Club. The main speaker of the evening was Paul V. McNutt, Dean of the Law School of Indianapolis University. The entertainment committee provided very interesting entertainment. 142 attended the banquet.

A meeting of the *Executive Committee* was held at the Severin Hotel, March 31, with the following members present: H. A. Winkelmann, E. H. Nahm, E. R. Bridgwater, N. G. Madge, H. F. Palmer, H. E. Simmons.

The purpose of this meeting was to discuss the question of raising finances for the expanding of RUBBER CHEMISTRY AND TECHNOLOGY. Several plans were proposed, and the following motion prevailed—Moved that the Division solicit funds for the purpose of creating a permanent endowment which will enable the Division to enlarge and expand RUBBER CHEMISTRY AND TECHNOLOGY.

Upon motion, the meeting adjourned.

H. E. SIMMONS, *Secretary-Treasurer*

Local Group Activities

Akron Group

February 9, 1931. Addresses by C. S. Powell (Firestone Tire and Rubber Co.) on "Recovery of Rubber and Cotton from Uncured Tire-Ply Scrap," by H. A. Brittain (Goodyear Tire & Rubber Co.) on "Drop Centre Tires and Rims," and by C. M. Carson (Goodyear Tire & Rubber Co.) on "Effect of Storage on Milled Crude Rubber."

Election of P. P. Crisp (Firestone Tire and Rubber Co.), Chairman, H. J. Conroy (General Tire and Rubber Co.), Vice-Chairman, L. W. Brock (Godfrey L. Cabot), Secretary-Treasurer.

April 20, 1931. Addresses by J. A. Nelson (U. S. A. Motor Transport, Detroit) on procurement in times of national emergency, by Harry Morris (Firestone Tire and Rubber Co.) on "New Methods of Masticating Rubber," and by H. E. Blythe (Goodyear Tire and Rubber Co.) on "Airships."

Boston Group

March 5, 1931. Addresses by Karl T. Compton (President of Mass. Inst. of Technology) on "The Relation of Science to Industry," and by H. L. Fisher (United States Rubber Co.) on "What Is New in Rubber Chemistry."

Chicago Group

December 5, 1930. Addresses by H. G. Bimmermann (E. I. du Pont de Nemours & Co.) on "Manufacture of Sponge Rubber," and by F. L. Dawes (Adamson Machine Co.) on "Tubing Machines."

May 8, 1931. Addresses by H. Bluhm and by A. H. Voss dealing with the manufacture and properties of hard rubber. Election of L. J. D. Healy, Chairman, W. H. Parker, Vice-Chairman, B. W. Lewis (Wishnick-Tumpeer, Inc.), Secretary-Treasurer.

Los Angeles Group

March 25, 1931. Address by F. D. Carpenter (United States Rubber Co. (Samson Div.), Los Angeles) on the Sumatra plantations of the United States Rubber Co. Election of F. S. Pratt, Chairman, P. A. Ritter, Vice-Chairman, and W. R. Hucks, Secretary-Treasurer.

New York Group

December 10, 1930. Address by Donald Laird (Colgate University) on "Smell in Rubber Goods as a Sales Resistance," and a motion picture of the manufacture of carbon blacks (described by D. F. Cranor, Binney and Smith Co.). Election of W. H. Whitcomb (H. L. Scott Co.) as new Chairman.

March 11, 1931. Addresses by E. K. Files (Lea Fabrics Co.) on "Manufacture of Carpets by a New Process Involving the Use of Unspun Fibres Organized to Fabric Backing" and by W. B. Wiegand (Binney and Smith Co.) on "The Effect of Overmilling on Natural Aging." J. P. Coe (Naugatuck Chemical Co.) was appointed Secretary-Treasurer.

May 20, 1931. Address by A. R. Kemp (Bell Telephone Laboratories) on "Rubber in the Telephone Industry."

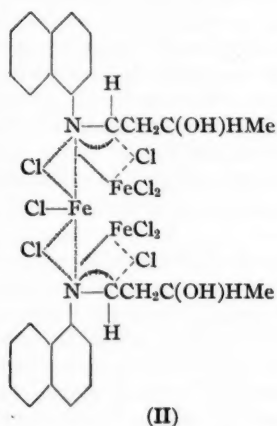
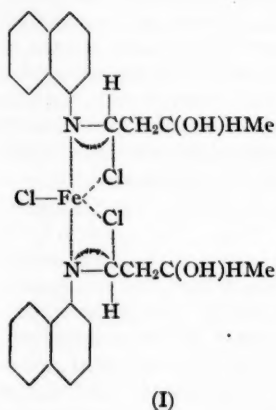
Report of the Treasurer of the Rubber Division April 2, 1931

Balance in the bank, September 4, 1930.....	\$1208.94	
(Reported at Cincinnati meeting)		
Dues and subscriptions to date (Mar. 30, 1931).....	1950.66	\$3159.60
Expenditures:		
Printing.....	\$93.89	
Stamps, telegrams, etc.....	27.36	
Expenses of H. E. Simmons (Cincinnati Meeting).....	59.00	

Deficit at banquet (Cincinnati Meeting).....	32.15	
Translations.....	218.40	
Stenographic services.....	30.00	
Refunds.....	17.00	
Rubber Age.....	70.64	
November Issue of RUBBER CHEMISTRY AND TECHNOLOGY	1236.67	1785.11
Balance in bank, March 30, 1931.....		\$1374.49
H. E. SIMMONS, <i>Treasurer</i>		

Correction

In an article entitled "The Protective Action of Some Antioxidants" by F. Kirchhof in the April, 1931, issue, there are on page 242 two formulas (Nos. I and II), from which certain valence bonds were omitted. These formulas should be as follow:



New Books and Other Publications

Government Control of Crude Rubber. By Charles R. Whittlesey. Published by the Princeton University Press, Princeton, N. J., 1931. 250 pp. \$2.50.

The scope of this volume is defined and also, unfortunately, limited by its subtitle, "The Stevenson Plan:" data and statistics brought down only to the close of 1928 do not adequately reveal the effects of this British effort at restriction. Even Wallace and Edminster a year earlier in their "International Control of Raw Materials" (Brookings Institution, 1930), were able to offer a picture of the situation after restriction had been lifted and to analyze some of its after effects. As a history of the period from 1922 to 1928, however, Mr. Whittlesey's study is comprehensive and of value as a reference manual, whether or not there can be agreement upon his "theoretical considerations" and conclusions. After presenting the background of the development of plantation rubber, he discusses the movement of prices and the administration of the plan and follows with an investigation of the effects upon the producing countries, the chief consuming country, and the investing country. He has exhausted a wide range of sources for his material and his data may be considered authoritative as well as complete, except for certain rare slips such as his citing as news item from this Journal of the organization of a company to manufacture mineral rubber as "a typical example of the numerous attempts to produce synthetic rubber" in competition with *Hevea Brasiliensis*.

An Economic View of Rubber Planting. By R. Soliva. Published by Kelly & Walsh, Ltd., Raffles Place, Singapore, 1930. Paper, 135 pages, 6 by 9 inches.

The author is a banker, who summarizes in this volume the information regarding the economic and financial aspect of plantation rubber production, gathered in his extended travels through Malaya, Java, Sumatra, Ceylon, and Indo-China. He regards the present slump in crude rubber prices as "the unavoidable repercussion of the previous extravagant boom." Mr. Soliva foresees that rubber planting must constantly improve its yields and lower its costs. He believes, moreover, that European planters are sufficiently progressive to compete with the native producer.

Malaya Rubber Statistics, 1930. Published by the Department of Statistics, Straits Settlements and Federated Malay States, Singapore, S. S., 1931. \$1 (Straits).

During 1929, separate booklets were issued by the governments of the Straits Settlements, the Federated Malay States, and Johore, which contained the results of the rubber statistical work done up to the end of 1928. The present booklet revises and amplifies these statistics and includes returns for the Unfederated Malay States up to the end of 1929, covering acreage, crops, imports, and exports. The better coördination of rubber statistical work in Malaya is reflected in this document, tables in which represent the combined work of the Department of Statistics, the Statistical Division of the Department of Agriculture, and statistics officers in the governments of the Unfederated States.

Markets for Machinery in British Malaya. By Don C. Bliss. Published by the United States Department of Commerce, Washington, D. C., 1931. \$0.20.

The British Malayan market for machinery covers a wide range but principally centers in the rubber processing and tin mining industries. The United Kingdom is the chief source of the colony's machinery imports, with the exception of power-generating and printing machinery. During the last five years, total machinery

imports into British Malaya have averaged around \$10,000,000, of which the United Kingdom accounted for about 60 per cent, European countries about 30 per cent, and the United States 10 per cent. Mr. Bliss, American trade commissioner at Singapore, recently completed a comprehensive survey of the British Malayan market for rubber processing and other machinery, the results of which are embodied in this bulletin.

Rutherford's Planter's Note Book. Useful memoranda for everyone connected with the planting industries of the Middle East. Ninth Edition. The Times of Ceylon Co., Ltd., Colombo, Ceylon, 1931. Cloth, 908 pages, 5 1/4 by 8 1/4. Indexed.

This is a compendium of information, of building, and mathematical data of great value to those in the planting industries such as tea, coffee, rubber, and coconuts. The data are supplemented with monographs on cultivation and manuring, fruit and shade trees, medical and legal information, insurance, animal diseases, electrical communication, and accounting.

Anatomie en Physiologie van Hevea Brasiliensis. By W. Bobilioff. Published by Ruygrock & Company, Batavia, Java, N. E. I., 1930. 288 pp.

A comprehensive and well illustrated discussion of the latex vascular system, the sections related to the numbers and diameters of latex tubes and their effect on latex yield being a review of the Ashplant controversy, is included in this treatise. Dr. Bobilioff was for many years one of the right-hand men of Prof. O. de Vries at the Central Rubber Testing Station in Java.

Standards Yearbook, 1931. Published by the National Bureau of Standards, United States Department of Commerce, Washington, D. C., 1931. 405 pp. \$1.00.

The more important activities of the Bureau of Standards in research and standardization are included in this annual publication. Among the investigations conducted during the year were those into the chemical nature of rubber, abrasion tests for rubber, antioxidants in rubber compounds, and the effect of humidity and temperature on the properties of rubber compounds.

Research Service for Industry. Engineering Research Circular No. 5, March, 1931. Department of Engineering Research, University of Michigan, Ann Arbor, Mich.

This circular aims to set forth the research service available through the Department of Engineering Research at the University of Michigan, as well as the conditions under which these services are made available. The nature of the problems and the scope of the service offered are outlined; while the research personnel and laboratory and library facilities also are enumerated.

Benzol Health Practices Pamphlet No. 14. National Safety Council, 20 N. Wacker Dr., Chicago, Ill.

This pamphlet describes the principles used in protecting the health of workers exposed to benzol.

Compounding Materials Used in the Rubber Industry—Part I. National Safety Council, 20 N. Wacker Dr., Chicago, Ill.

This industrial safety pamphlet is devoted to accelerators, antioxidants, and dry organic compounds. It is designated as Industrial Safety Series No. Ru. 1 and is a compilation of experience in accident prevention, which should be studied by every rubber chemist, technologist, compounder, and superintendent.

Notes on the Carbon-Black Flame. By W. B. Wiegand. Published by the Binney & Smith Company, 41 East 42nd Street, New York City, 1931. 10 pp. For free distribution.

The basic difference between carbon black and lamp black is defined in terms of the method of collection in this paper, which was originally read before the Rubber Division of the American Chemical Society at last September's meeting in Cincinnati. Possible causes of the unique properties of impingement black are discussed. By reference to two types of carbon black flames—round and flat—the conception of "combustion quotient" is developed and applied to variations in flame size and shape, and to drafting. The position of the impingement surface, the effect of flame shape, of gas flow, and of position of channel are briefly discussed in relation to the quality and quantity of black obtained. Factors of importance in large scale operations are mentioned.

A Survey of Recent Literature on the Chemistry of Rubber

Abstracts of Articles Pertaining to the Chemistry of Rubber Which Have Appeared in Foreign and American Journals

The following abstracts are reprinted from the March 10 and 20, April 10 and 20, May 10 and 20, and June 10 and 20, 1931, issues of *Chemical Abstracts* and, with earlier and succeeding issues, they form a complete record of all chemical work published in the various academic, engineering, industrial, and trade journals throughout the world.

Rubber. Newer theoretical and practical developments. HARRY L. FISHER. *J. Chem. Education* 8, 7-29(1931).—An illustrated review and discussion dealing with latex, non-rubber components, the rubber hydrocarbon and its purification, chem. derivs. of rubber, the phys. structure of rubber, vulcanization, acceleration, aging and practical developments. C. C. DAVIS

Laboratory methods in a rubber factory. T. W. FAZAKERLEY. *Caoutchouc & gutta-percha* 27, 15307-8(1930).—A discussion of lab. costs. C. C. DAVIS

Further rubber pigments. F. HARRIS COTTON. *India Rubber J.* 80, 865-6(1930); cf. *C. A.* 25, 841. C. C. DAVIS

A method of estimating with methylene blue the adsorption power of commercial carbon blacks. Other properties of blacks. R. DITMAR AND K. H. PREUSSE. *Rubber Age* (London) 11, 416-8(1931).—English version of *C. A.* 25, 842. C. C. DAVIS

Fillers and their functions. V. Oil substitutes. F. HARRIS COTTON. *India Rubber J.* 80, 411-3(1930); cf. *C. A.* 25, 841. C. C. DAVIS

The manufacture of synthetic molding powders. F. A. BATH. *Rev. gén. caoutchouc* 7, No. 66, 19-21(1930).—A review and discussion of general problems. The pressure used in molding is considered to be the most important factor in manuf. C. C. D.

The plasticizing of rubber. F. JACOBS. *Rev. gén. caoutchouc* 7, No. 66, 9-14 (1930); cf. *C. A.* 25, 840.—The discussion includes various French softeners and wood tars and resins. C. C. DAVIS

Behavior of antioxidants in rubber stocks containing copper. PAUL C. JONES AND DAVID CRAIG. *Ind. Eng. Chem.* 23, 23-6(1931).—The expts. deal with the behavior of antioxidants of various types (paraffin wax, 4,4'-diaminodiphenylmethane, *N,N'*-di-*p*-tolyl-1,2-ethylenediamine, phenyl- α -naphthylamine, phenyl- β -naphthylamine, *N,N'*-diphenyl-*p*-phenylenediamine, *N,N'*-di- β -naphthyl-*p*-phenylenediamine, aldol- α -naphthylamine and tetraphenylhydrazine) in vulcanizates of different comps., each of which was cured with and without Cu stearate. The aging effects were observed by natural storage in darkness, by heating in air at 70° and by heating in O under 300 lb. per sq. in. pressure at 70°. The results show that some of the antioxidants retarded the deterioration caused by the Cu stearate. In this respect the secondary aromatic amines were by far the most effective. In general, however, it is difficult to distinguish clearly the relative effects of different antioxidants on the phys. changes during aging because of differences in the effect of the different antioxidants on the rate of vulcanization. The effects obtained with some of the antioxidants warrant their use in practice where rubber products undergo extensive oxidation as a result of the action of Cu or Cu compds., e. g., when they are in contact with brass. C. C. DAVIS

Mechanical properties of rubber in compression at low temperature. W. D. DOUGLAS. *India Rubber J.* 80, 899-901(1930).—A study of the stress-strain curves of the compression of cured rubber at 20°, 10°, 0°, -10°, -20°, -30°, -40° and -50°. The method and technic are described and the results are recorded graphically. The stress-strain curves include both static and dynamic deflections. C. C. DAVIS

Toxic substances in the rubber industry. XVIII. Hydrogen sulfide. P. A. DAVIS. *Rubber Age* (N. Y.) 28, 405-6(1931); cf. *C. A.* 25, 843.—H₂S is so toxic

that it should be classed with HCN and CO, and where it is a const. factor the operations should be in a closed system and the H_2S eventually burned. The concn. in the open should be below 0.01 part per 1000. C. C. DAVIS

Rubber in the shoe industry. G. DUMONTIER. *Rev. gén. caoutchouc* 7, No. 66, 31-2(1930).—A general discussion with representative formulas. C. C. DAVIS

The manufacture of rubber belts. THOS. FAZAKERLEY. *Rev. gén. caoutchouc* 7, No. 66, 15-7(1930).—A general description, with representative rubber formulas. C. C. DAVIS

Testing of railway brake and heating hose. ANSELM TALALAY. *India Rubber J.* 81, 21-2(1931).—The specifications of the German State Railways are described and illustrated. C. C. DAVIS

Flax versus cotton in tire fabric construction. H. WALTER GROTE. *Rubber Age* (N. Y.) 28, 355-6(1931).—A new process for defibration of flax fiber may make linen a substitute for cotton fabric in tires. C. C. DAVIS

Accelerators of vulcanization. F. JACOBS. *Caoutchouc & gutta-percha* 27, 15258-62 (1930); cf. *C. A.* 25, 233.—The accelerators include certain amines and guanidines. C. C. DAVIS

Modern accelerators and their capabilities. F. HARRIS COTTON. *India Rubber J.* 80, 481-2, 605-7(1930).—A review and discussion. C. C. DAVIS

Vulcanization accelerators. A survey of the patent literature of the last few years. VI. ALADIN. *Gummi-Ztg.* 45, 153(1930); cf. *C. A.* 25, 233.—The tabulated data and information are concluded with a total of 227 accelerators. C. C. DAVIS

The adsorption theory of the combination of sulfur during vulcanization. WOLFGANG OSTWALD. *Gummi-Ztg.* 44, 1743(1930).—A criticism of certain features of a book by Kindscher (*Handbuch der Kautschukwissenschaft*). C. C. DAVIS

The adsorption theory of the combination of sulfur during vulcanization. HEINRICH LOEWEN. *Gummi-Ztg.* 45, 622(1931).—Comments on a paper by Ostwald (cf. preceding abstr.). C. C. DAVIS

Hot vulcanization. PAUL BREDEMANN. *Gummi-Ztg.* 45, 502-3(1930); cf. *C. A.* 25, 843. C. C. DAVIS

Studies of the conditions affecting the vulcanization of rubber. V. The effect of accelerators on the heat of vulcanization. Y. TOYABE. *J. Soc. Chem. Ind., Japan* 33, Suppl. binding 275-6(1930); cf. *C. A.* 24, 3397.—The heats of vulcanization of rubber mixts. contg. different proportions of S and 10 different accelerators, resp., were measured by means of a differential thermocouple. The course of the curves was similar to that of the curves with unaccelerated mixts., but the temp. maxima occurred sooner with the accelerated than with the unaccelerated mixts. The expts. show that these accelerators promote the disaggregation of micellar structure of rubber, as shown in the previous expts. (cf. T., Fukunaga and Fukuda, *C. A.* 24, 4664; T. and Fukunaga, *C. A.* 24, 4664) before the chem. combination of rubber and S. By reducing the size of the individual rubber micelle, they increase the no. of chem. units of rubber entering the reaction with S, i. e., the probability of combination of the two becomes greater. The time at which the temp. maxima appear in the expts., which is shortened by accelerators, shows that this theory holds good if it is considered that the temp. maxima correspond to the disaggregation maxima of the rubber hydrocarbon in question. C. C. D.

The rubber industry in 1930. S. A. BRAZIER. *Ind. Chemist* 7, No. 72, 9-12(1931). E. H.

Structure viscosity of rubber solutions. B. DOGADKIN AND D. PEWSNER. *Kolloid-Z.* 53, 239-45(1930).—The viscosities of pale crepe, smoked sheet and milled rubber solns. in C_6H_6 at 15°, 25° and 45° were measured at varying pressures. Deviations from the Hagen-Poiseuille law were checked. The results may be expressed by the Waele-Ostwald formula: $\eta = KP^{1-n}$. The exponent n of this equation may be used as a measure of structural peculiarities of different rubbers and it characterizes various changes in the aggregation of rubber. With increasing temp., n increases with diminution in viscosity. Milling, which represents colloid-chem. processes of disintegration, causes a large decrease in the structure viscosity exponent. A similar process occurs in the aging of rubber solns. ARTHUR FLEISCHER

Micromanipulations on latex in dark fields. E. A. HAUSER. *Kolloid-Z.* 53, 78-82 (1930).—New investigations have confirmed the previous results of Freundlich and H. (cf. *C. A.* 19, 2280). For latex from trees of different age, the thickness of the solid layer of the latex particle increases with the age of the tree. By coagulation of the latex, particles with noticeable elastic properties are obtained, in which the consistency of the inner and outer layers is not distinguishable. ARTHUR FLEISCHER

Determination of p_H of ammonia latex. J. MCGAVACK AND J. S. RUMBOLD. *Ind.*

Eng. Chem., Anal. Ed. 3, 94-7(1931).—Details of expts. are given in which the p_H of latex was detd. at various NH_3 concns. by the use of indicators and with the glass electrode. The 2 curves thus obtained were comparable but not identical. The glass electrode method gives results which are reproducible and accurate up to p_H 9.5, and which are fairly accurate up to p_H 11.0. In more alk. solns. it is necessary to carefully calibrate each electrode. An ordinary galvanometer gave satisfactory results with potentials down to 1 millivolt, and the asymmetry of the glass was negligible.

W. T. H.

The constitution of rubber. R. PUMMERER. *Kolloid-Z.* 53, 75-8(1930).—A chem. method is needed to decide whether the rubber mol. is a system of closed isopentene rings or is a long chain mol.

ARTHUR FLEISCHER

Solvent action in rubber. P. STAMBERGER AND C. M. BLOW. *Kolloid-Z.* 53, 90-5(1930); cf. *C. A.* 23, 4846.—Osmotic pressure detns. of rubber solns. in toluene at 25° checked the older results of Posnjak, though the rubber samples were from entirely different sources. The plot of $\log P$ against $\log c$ for the equation $P = P_0 c^K$ does not give a straight line, showing that K changes with the concn. There is no difference between the osmotic pressure of gels and solns. Different rubbers gave the same values of the osmotic pressure at like concns. The viscosity-pressure diagrams of petr. ether and benzene solns. of milled rubber were not very different, though optically they were quite different. The viscosity curves of solns. of dead-milled rubber, the same rubber with 15% of gas black dissolved at once and after 30 days, showed increasing viscosities in the above order. These solns. were thixotropic.

ARTHUR FLEISCHER

The fusion curve of natural rubber. G. v. SUSICH. *Naturwissenschaften* 18, 915-6(1930).—Previously frozen raw rubber has a "m. p." at 35-8°. The crystal interferences in the x-ray diagram disappear at this temp. and the rubber becomes elastic. High stretching raises this m. p. A diagram is given of elongation vs. temp., in which the m.-p. curve is shown. Crystn. is characterized by the initial appearance of the (200) interference. For 1000% elongation the m. p. is between 80° and 90°.

B. J. C. VAN DER HOEVEN

Rubber preservatives. RUDOLF DITMAR. *Chem.-Ztg.* 54, 994-6(1930).—A review, with particular reference to the many patented substances.

C. C. DAVIS

Determination of alkalinity of reclaimed rubber. HENRY F. PALMER AND GEORGE W. MILLER. *Ind. Eng. Chem., Anal. Ed.* 3, 45-8(1931).—A new method for detg. the relative alk. of reclaimed rubber is described, and compared with an earlier method already described (cf. *C. A.* 22, 1058). The alkali is extd. by digestion of the reclaimed rubber in a mixt. of $EtOH$, C_6H_6 , and water. The expts. show that the new method gives reliable results, which are approx. 4 times as precise as those of the previous method. This greater precision is a result of the elimination of much of the personal error, of extn. of a larger proportion of alkali, and of a closer end point in the titration.

C. C. D.

Overflow during vulcanization of rubber and its results. F. KIRCHHOF. *Chem.-Ztg.* 54, 906-8(1930).—A criticism of a paper by Ditmar and Preusse (cf. *C. A.* 24, 5179-80) with certain new data on the expansion of rubber mixts. during vulcanization. These new data, in conjunction with the results of D. and P. and other investigators, lead to certain conclusions. (1) Raw rubber and rubber mixts. show in the temp. interval between room temp. and the temp. of vulcanization considerable evolution of heat. (2) The d. of raw rubber and rubber mixts. is, within narrow limits (2-3 decimals), dependent upon the time and temp. of mastication. (3) Upon storage the d. increases as a result of reaggregation. (4) Soft vulcanization in principle involves a contraction of vol., i. e., an increase in d. Under normal conditions this increase is about 2.0% (calcd. on the unvulcanized mixts.). (5) Hard-rubber vulcanization likewise involves a contraction of vol., i. e., increase in d., which may reach 6%. (6) The pressure used in vulcanizing increases the d., and this is of the same order of magnitude as the increase resulting from reaggregation. (7) Certain active fillers (heavy metal oxides and sulfides) when in large proportions have a similar contractive effect to small proportions of Se or considerable S. (8) These effects are probably attributable to capillary or affinity forces. (9) The overflow which takes place during vulcanization in a press is chiefly the result of purely mech. factors (compression) but is to some extent a result of heat expansion and vol. contraction.

C. C. DAVIS

The rubber industry in the United States. L. P. MAX. *Rev. gén. caoutchouc* 7, No. 65, 3-6; No. 66, 3-8(1930).

C. C. DAVIS

A few facts on the study of rubber-bearing plants of the Russian Soviet Republic. SERGIUS IVANOV, T. S. CHELZOVA, S. B. RESNIKOVA, E. I. TROFIMOVA, E. M. DUHNE AND V. I. SVESHNIKOVA. *Kautschuk* 6, 237-9, 256-8(1930).—The results of an investigation of over 150 plants are described, with analytical data tabulated in detail.

The most promising raw material was the rubber of the *Chondrilla*, the "naphivi" of which with suitable improved methods yield considerable rubber. C. C. DAVIS

The significance of the primary valence chain theory in explaining the structure of rubber. EUGENIO LINDMAYER. *Kautschuk* 6, 249-52(1930); cf. C. A. 24, 750.—A review and discussion. C. C. DAVIS

The plasticizing of rubber. F. JACOBS. *Rev. gén. caoutchouc* 7, No. 67, 19-26 (1930); cf. C. A. 25, 1117.—Various wood resins, tars, pine tars and oils are described and discussed, with quant. data (already published). C. C. DAVIS

An aging test with kerbosch rubber. R. RIEBL. *Arch. Rubbercultuur* 14, 411-20 (1930) (In briefer form in English 421-4).—Kerbosch rubber and latex-sprayed rubber were kept at av. temps. of 27° and 18° (at places with different climates) to ascertain the influence of different climatic conditions on the aging of both types of whole latex rubber. The Kerbosch rubber deteriorated badly at sea level, but nowhere nearly so rapidly at 5000 ft. elevation (cf. de Vries, C. A. 18, 2265). The latex-sprayed rubber aged much better than the Kerbosch rubber, and furthermore the aging of the former was not so disproportionately bad at sea level. The results in general show the important influence of climate on the aging of rubber of the Kerbosch type. C. C. D.

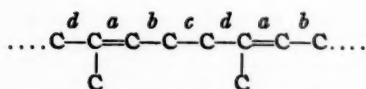
Manufactured rubber, its keeping qualities and reconditioning. P. BRUÈRE. *Arch. méd. pharm. militaires* 91, 571(1929); *J. pharm. Alsace Lorraine* 57, 219-28 (1930); cf. C. A. 24, 3397. S. WALDBOTT

The Kelly abrasion machine. A. F. HARDMAN, W. L. MACKINNON AND S. M. JONES. *Rubber Age* (N. Y.) 28, 463-5(1931).—The new machine, which is described and illustrated, is designed to simulate the road wear of tires, with special attention to 3 factors: (1) increasing and diminishing pressure of contact of the rubber with the abrasive material, (2) application of only part of the surface to the abrasive material and (3) a side slip as the rubber leaves the abrasive surface. With this method, actual road wear can be foretold reliably. C. C. DAVIS

Modern methods of cycle tire vulcanization. A. FRÖLICH. *Gummi-Ztg.* 45, 543 (1930); *India Rubber J.* 81, 154-7(1931).—An illustrated description. C. C. DAVIS

The oil and the lipase-like enzyme in Para rubber seed. YOSHITORA IWAMOTO. *J. Soc. Chem. Ind., Japan* 33, Suppl. binding 409-11(1930).—Fallen seeds from Malaya were used in the expts. The following data give the kind of seed, the grade of oil from each kind, the color of the oil, its taste and its acid no., resp.: fresh with yellow-white kernel, 1st, faint yellow, sweet, 7.21; older with dirty yellow kernel, 2nd, yellow, bitter, 24.71; partly putrefied, 3rd, brownish yellow, bitter, 77.10; badly putrefied with dark gray kernel, 4th, brown, very bitter, 110.86. The results show that fresh seeds are suitable for practical oil extn. Oil obtained by cold-pressing is superior to oil by hot-pressing, as shown by a higher yield, a lighter color, a sweeter taste and a much lower acid no. (19.70 vs. 45.22). A bitter taste is best removed by NaOH. Oil extd. with petr. ether from fresh seeds showed d_4^{20} 0.9234, n_{20} 1.4757, acid no. 7.12, I no. 138.8, solidifying point 2°, sapon. no. 189.20, Reichert-Meissel no. 2.28, acetyl no. 2.41, unsaponifiable matter 1.62, insol. hexabromide (fatty acids) 15.48. By the Pb salt-Et₂O method, the fatty acids yielded 79.99% of yellow liquid acids and 17.81% of white solid acids. The former when oxidized with alk. KMnO₄ by the Hazura method gave dihydroxystearic, sativic and linusic acids. This shows that the liquid acids contain considerable oleic, linolic and linolenic acids. After recrystn. from 95% EtOH at -20°, the solid acids yielded a white cryst. powder which m. 62° and had a neutralization no. 204.62, which was probably a mixt. of 70% stearic acid and 30% palmitic acid. The high acid no. of the oil from decayed seeds suggested the presence of lipase. The following data give the acid nos. of the oils extd. with Et₂O from 4 samples before and after 92 days at room temp., resp.: (1) seeds with husks, 5.41, 15.72; (2) crushed kernel with husk removed, 6.30, 48.82; (3) crushed kernel with oil removed and then ground with rapeseed oil, 1.20, 93.37; (4) same as (3) but with kernel previously heated 5 hrs. at 105° before adding rapeseed oil, 1.20, 8.24. In tests of the lipolytic properties of kernels, pos. results were always obtained. It is suggested that the oil from fresh seeds might be used in food products, but it is more suitable for low grades of soap, for oil hardening and in conjunction with other oils in paint. C. C. DAVIS

Natural and synthetic rubber. VI. The pyrolysis of natural rubber in the presence of metallic oxides. THOMAS MIDGLEY, JR., AND ALBERT L. HENNE. *J. Am. Chem. Soc.* 53, 203-4(1931); cf. C. A. 24, 3129.—Pale crepe rubber pyrolyzed in the presence of ZnO or MgO gives the same decompn. products as in the absence of these oxides, but in different proportions. If the rubber mol. is represented by a long open-chain formula, the various bonds being designated by the letters, a, b, c, d, the relative ruptures during pyrolysis of straight rubber are represented by the values:



$a = 0, b = 0.6, c = 100, d = 0.7$; in the presence of MgO the values are $a = 0, b = 12.7, c = 100, d = 12.1$. This modification is attributed to an action of the oxides upon the double bonds of the rubber mol.

C. J. WEST

Report on the effect on the plasticity of crepe of adding sodium bisulfite to latex. G. MARTIN AND L. E. ELLIOTT. *Trop. Agr. (Ceylon)* 75, 213-5 (1930).—Samples of crepe contg. variable proportions of NaHSO₃ were tested for hardness and plasticity. Hardness is proportional to the NaHSO₃ added. The normal quantity of NaHSO₃ increases the mastication no. about 15% over that without it. The temp. of storage has little effect on the hardness or plasticity. Addns. of NaHSO₃ do not appear to increase the total mineral matter in the rubber but do make it more hygroscopic. The increased hardness cannot be due to the extra H₂O, since moist rubber does not harden as much as dry rubber on keeping.

A. L. MEHRING

The preparation of plantation rubber. G. MARTIN. *Bull. Imp. Inst.* 28, 440-50 (1930).—A description is given of the methods of prepn. of plantation rubber used in Ceylon, Malaya and Java, with tables to show the differences in detail between the procedures followed in the 3 countries. Also in *Trop. Agr. (Ceylon)* 76, 18-26 (1931).

A. PAPINEAU-COUTURE

Liquid rubber compounding. WEBSTER NORRIS. *India Rubber World* 83, No. 5, 53-5, 64 (1931).—An illustrated description of recent developments in the preservation, diln., stabilization and neutralization of latex, mixing operations, typical compds. and industrial applications.

C. C. DAVIS

Action of nitrogen oxide on rubber. ADOLF GORGAS. *Ber.* 63B, 2700-5 (1930).—Various observers have reported the formation of definite products by the action of NO₂ on rubber (Weber, C₁₀H₁₈N₂O₄; Emden, C₁₀H₁₆N₂O₆; Harries, Alexander, products of more complex compn.). These workers paid no particular attention to the purity of the NO₂. The best results were obtained with the gaseous decompn. products of Pb(NO₃)₂; Emden used the product obtained from HNO₃ and starch. G., on the other hand, carefully purified his NO₂, which was prepd. from HCHO and concd. HNO₃. The resulting mixt. of N₂O₃ and N₂O₄ was liquefied in a freezing mixt., completely converted into N₂O₄ with air, frozen, repeatedly crystd. and fractionated by distn. For the reaction with rubber the N₂O₄ was used in CCl₄ soln. satd. at room temp. Total rubber, prepd. from "Revertex" according to Pummerer and Pahl by treatment with alkali at 50° and subsequent dialysis, was used in 1% soln. in CCl₄. This rubber, as has been described elsewhere (C. A. 23, 1525), gave by the modified Hanus method I nos. agreeing well with the calcd. values, and the sol and gel rubbers prepd. from this total rubber also gave normal I values (1 mol. I per C₅H₈ group). Contrary to Pummerer and Mann, G. found for the gel rubber with BrI an I no. about 10% too low instead of too high. By the Kaufmann (SCN)₂ method, the 2 rubbers showed no appreciable difference. The nitrosation was effected by adding the rubber soln. to 5 parts of the N₂O₄ soln. at 0° and letting the mixt. stand 15 min. in 1 series of expts. and 24 hrs. in another. The compn. of the resulting products did not correspond to any of the formulas given by earlier workers, even after pptn. from Me₂CO with Et₂O, and the expts. showed decisively that abs. pure NO₂ does not form homogeneous products with purified rubber. As already pointed out by Alexander, the addn. of NO₂ is accompanied to a considerable extent by oxidation. The addn. reaction apparently does not give NO₂ derivs.; at least, G. has thus far been unable to effect a reduction to NH₂ derivs., but he did observe that when the product of the 24-hr. treatment with NO₂ is heated with concd. alkali, about 1/2 of the N is split off as NH₃, which makes it probable that the N is present as an NOH group (probably as an isonitroso ketone). In view of the strongly oxidizing action of NO₂, expts. were made with NO. As it reacts much more slowly than NO₂, the well-purified NO was passed for 4 hrs. through a very dil. soln. of rubber in CCl₄ at 20°. The product was non-pulverizable, and had a compn. (about C₁₄H₁₂N₂O₁₀), indicating that oxidation to a marked degree accompanied the addn. reaction. The product was also no more homogeneous or const. in compn. than that obtained with NO₂, and gave NH₃ with hot concd. alkali. With HNO₃ it is possible to keep the 2 reactions sep. Dil. HNO₃ and rubber give a N-contg. product which, however, is partially insol. in Me₂CO, and this insol. portion is N-free while the N in the sol. portion is split off as NH₃ by boiling alkalies. The formation of the N-contg. product can be prevented by complete removal with urea of the HNO₃

which is formed. The yellow pulverizable product is sol. in PhNO_2 , PhNH_2 , and dil. alkalis. G. hopes soon to be able to report its compn., mol. wt., etc. C. A. R.

The rubber era. T. L. GARNER. *India Rubber J.* 80, 643-8(1930).—An illustrated description is given of modern technical applications of rubber. C. C. DAVIS

The trend of American rubber development research. ARNOLD S. SMITH. *India Rubber J.* 80, 664-7(1931).—An English version (slightly abbreviated) of C. A. 24, 4954. C. C. DAVIS

Industrial uses of rubber. H. E. FRITZ. *Paper Mill* 54, No. 3, 14, 16-7(1931).—An outline of the widening applications of rubber rendered possible by the discovery of the Vulcalock process of bonding rubber to metal, which permits of utilizing to better advantage the corrosion-resisting and abrasion-resisting qualities of rubber. A. P.-C.

Preparation of sheet rubber. R. O. BISHOP. *Malayan Agr. J.* 19, 14-21(1931).—A discussion is given of present-day methods for the collection and handling of latex, its coagulation, handling of the coagulated rubber and drying and packing of the rubber. C. C. DAVIS

Toxic substances in the rubber industry. XIX. Sulfur and its derivatives. P. A. DAVIS. *Rubber Age* (N. Y.) 28, 513-4(1931); cf. C. A. 25, 1117.—With proper ventilation, choice of individuals and cleanliness, no trouble is likely with S. Fifteen yrs.' experience showed no serious cases of conjunctivitis, dermatitis, etc., from exposure to S. C. C. DAVIS

Technical note on the use of certain solvents in solutions. H. COULANGEON. *Caoutchouc & gutta-percha* 27, 15274-6(1930).—When a film of cement dries, the evapn. of the solvent causes a lowering of the temp., which may be great enough to reach the dew point and thus cause moisture deposit on the rubber. This results in poor adhesion when the surfaces are united. Since the lowering of the temp. varies with the solvent, it is possible to avoid this condensation of moisture by the proper choice of solvent for the conditions. Data were obtained on the lowering of temp. (wet bulb) of cements of the same viscosity made with solvent naphtha, toluene, aviation gasoline and benzene, resp., with the atm. at different temps. (10-30°) and humidities. By plotting the results graphically, the resulting chart shows under what conditions of temp. and humidity cements made with the various solvents can be used successfully without recourse to warming, and under what conditions and to what extent warming is necessary. C. C. DAVIS

Paragutta, a new insulating material for submarine cables. A. R. KEMP. *J. Franklin Inst.* 211, 37-57(1931).—Gutta-percha and balata have proved themselves eminently suitable for insulating long deep-sea telegraph cables, but their dielec. losses are too high to meet the requirements of submarine telephone cables for long distances or for shorter cables with carrier currents. Accordingly an extensive investigation was made of the causes of elec. defects of submarine insulation, including a search for an improved material. One result was the development of a new material called *paragutta*, and the present paper describes its properties and tests for detg. its utility. *Paragutta* consists essentially of the purified balata or gutta-percha hydrocarbons, with a small proportion of waxes. In developing this mixt., it was necessary first to purify the rubber, especially to remove proteins, in order to increase its elec. stability on prolonged immersion in water. Rubber from which water-sol. substances have been removed absorbs no more water than does gutta-percha (cf. Williams and K., C. A. 21, 1372; Lowry and Kohman, C. A. 21, 1372; Boggs and Blake, C. A. 20, 2092), but when immersed in water it fails completely as an insulator. To explain this elec. instability, rubber hydrocarbon freed of proteins, resins and other impurities was prepd. and tested. The product absorbed very little water, and on prolonged immersion in water it showed practically no change in elec. properties. Many expts. showed that the only practical method for removing proteins from rubber is to heat the rubber in an autoclave in water alone, which hydrolyzes the proteins to water-sol. products. Subsequent washing removes nearly all N. Sheet rubber or latex can be used for prepg. N-free rubber in this way. Thus ammoniated latex is diluted by addn. of 4 vols. of water, heated 10 hrs. at 150° in an autoclave, cooled, coagulated with AcOH, washed thoroughly and dried. The N content is then under 0.1%. When vulcanized, this deproteinized rubber is superior to ordinary rubber in its elec. stability in water. The deproteinized rubber is also more easily plasticized and mixed with gutta-percha than is ordinary rubber. *Paragutta* is prepd. by blending deproteinized rubber with purified gutta-percha hydrocarbon, with the optional addn. of special hydrocarbons or montan wax. The proportions of the 3 components may be varied to suit the conditions. Thermoplastic insulators thus prepd. are almost like gutta-percha in mech. and elec. properties in water, and they are cheaper. Data show tensile, compression, flexibility, plasticity, brittleness, water absorption and elec. tests of *paragutta* in comparison with gutta-

percha. These data prove conclusively that paragutta behaves in almost the same way as gutta-percha in all these respects. It has the desirable thermoplastic and mech. properties of gutta-percha, and its superior insulating properties render it particularly adapted for transoceanic telephone cables. Paragutta is also of advantage for shorter deep-sea carrier telephone cables and for ocean telegraph lines. C. C. DAVIS

Reconditioning air bags by burning. CHARLES E. MAYNARD. *Chem. Met. Eng.* 38, 91; *Rubber Age* (N. Y.) 28, 565(1931).—A new machine is described for reconditioning air bags used in the vulcanization of rubber tires. It removes the hardened surface layer of used bags by burning and scraping, thus leaving a smooth surface and thoroughly reconditioning in one operation. C. C. DAVIS

Accelerators of vulcanization. Mercaptobenzothiazole. F. JACOBS. *Caoutchouc & gutta-percha* 28, 15350-4(1931); cf. *C. A.* 25, 1118.—The prepn. and properties of mercaptobenzothiazole are described, including its behavior and utility in rubber mixts. **Mercaptides.** *Ibid* 15394-6.—By mercaptides are meant combinations of mercaptobenzothiazole with other accelerators having basic properties, e. g., with hexamethylenetetramine, diphenylguanidine, di-*o*-tolylguanidine and ethyldeneaniline. The behavior of some of these com. substances as accelerators is described, with examples to show their utility. C. C. DAVIS

Oxidation of vulcanized rubber mixtures extracted with acetone. T. YAMAZAKI AND K. OKUYAMA. *Caoutchouc & gutta-percha* 28, 15359-60(1931).—See *C. A.* 24, 4664. C. C. DAVIS

The chemical technology of rubber. SIDNEY M. HAGMAN. *Reprint from Svenska Gummi Ind. Memorial Number*, issued on the occasion of Disponent Henry Dunkers' 60th anniversary, September 6, 1930.—A general discussion. H. C. DUUS

A modern service laboratory—the I. C. C.'s work for the rubber industry. ANON. *Chem. Trade J.* 52, 100-1(1931).—A description is given of the new service lab. for the rubber industry that has been equipped by the Brit. Dyestuffs Corp., Ltd., at Hexagon House, Blackley, near Manchester. One section deals with the solution of technical problems, the second with the routine testing of rubber industry chemicals and colors and the third with research. W. H. BOYNTON

The world's rubber supplies. GEO. RAE. *Bull. Rubber Growers' Assoc.* 13, 59-84 (1921).—Though chiefly economic, the paper is of general interest, as it deals with planted areas, output, exports, imports, consumption and stocks in the producing and mfg. localities. C. C. DAVIS

Metallurgical methods used in producing rubber. PAUL D. V. MANNING. *Chem. Met. Eng.* 38, 131-2(1931).—An illustrated description is given of new machinery for planting, cultivating and prepg. guayule. C. C. DAVIS

Patents and custom standards of new machines for the manufacture of rubber articles. RUDOLF DITMAR. *Kolloid-Z.* 54, 237-9(1931).—A review. A. FLEISCHER

The use of pigments in the rubber industry. FERD. A. RICHTER. *Farbe. u. Lack* 1931, 135.—The primary use of pigments in rubber is not for the color but for the phys. properties imparted to the rubber. The choice of pigment depends upon the method of vulcanization as well as the use to which the product is put. G. G. SWARD

Reënforcing action of pigment mixtures on rubber compounds. D. J. BEAVER AND J. W. MACKAY. *Ind. Eng. Chem.* 23, 294-6(1931).—The exptl. data which are presented show that mixts. of varying proportions of either channel gas black or a "soft" C black with whiting, lithopone or clay impart additive phys. properties to the vulcanizate. Mixts. of "soft" C black with ZnO also impart additive properties, whereas mixts. of channel black with ZnO result in poorer resistance to abrasion, in a higher modulus and in a higher tensile strength than those corresponding to the additive effects. These facts are explained by a chem. reaction between the basic ZnO and the acidic compds. in the rubber or on the C black. These results are applied to the formulation of a solid tire rubber mixt., which shows a greater resistance to abrasion and to "blow-out" when it contains a "soft" black than with a channel gas black. C. C. D.

American-grown rubber produced from guayule. GEO. H. CARNAHAN. *Chem. Met. Eng.* 38, 128-31(1931).—An illustrated description of recent developments (cf. Spence, *C. A.* 24, 2914). C. C. DAVIS

Physical tests of sponge rubber. F. L. HAUSHALTER. *India Rubber World* 83, No. 5, 59-60(1931).—An *app.* to measure the compressibility and the permanent set after compression of sponge rubber is described and illustrated. C. C. DAVIS

Soft rubber in chemical process equipment. H. E. FRITZ. *Chem. Markets* 28, 273, 275, 277(1931).—An illustrated description is given of the application of rubber to ball mill linings, and machinery bearings, with special reference to the Vulcalock process. C. C. DAVIS

Chemical constitution of rubber. MARIO D. PINTO. *Rev. brasil. chim.* 2, 267-70 (1930).—P. discusses the work of the early investigators, and shows the evolution of the present formula $(C_4H_8)_n$.

JOHN M. LADINO
Isoprene and rubber. XXII. Isorubber-nitrone. H. STAUDINGER AND H. JOSEPH. *Ber.* 63B, 2888-99 (1930); cf. *C. A.* 24, 4954.—Pummerer's view that the unit mol. of rubber is $(C_4H_8)_n$ is supported by mol.-wt. detns. on rubber in menthol and especially on isorubber-nitrone (I) in C_6H_6 and $PhNO_2$. These results, which have been confirmed as to their order of magnitude, are apparently not in agreement with Staudinger's view, based on model expts. with polystyrenes, the conversion of rubber into colloid-sol. rubber-phosphonium salts, the prepn. of polymer-homologous series of polyrenes, the degradation of rubber, the relationship between viscosity and mol. wt., etc., all of which lead to the conclusion that the primary colloid particles of rubber, *i. e.*, the particles in dil. soln., are macromols. contg. some 1000 isoprene mols. joined in a chain (mol. wt. around 68,000). A study of the action of $PhNO$ on rubber solns. gave results somewhat different from those of Pummerer and Gündel. They believed that the resulting decrease in viscosity is due to the disturbance of the rubber micelles. It has been found, however, that the viscosity of solns. of macromol. (eucolloid) polystyrene is greatly diminished by Cl , Br , strong oxidizing agents (N oxides, O_3), etc., as the result of an irreversible cleavage of the long sensitive macromols. into shorter fragments having a hemi-colloid character. The viscosity changes (often considerable) produced in highly viscous rubber solns. by the addn. of reagents are also irreversible, and therefore cannot be due to adsorption of the reagent on the colloid particles or to changes in their micellar structure. The macromols. of rubber, because of their double bonds, are much more sensitive than the satd. macromols. of polystyrene, and their cleavage into shorter fragments of hemi-colloidal character is a primary phase of almost all transformations undergone by rubber. To det. the extent of such a cleavage in the reaction with $PhNO$, varying quantities (0.01-3.0 mols.) of $PhNO$ were added to a 0.2 *M* soln. of rubber (purified according to Pummerer) in C_6H_6 , and after 24 hrs. at 20° the time of flow from an Ostwald viscometer was noted. Parallel expts. were made with NO_2 and Bz_2O_2 . Below are, resp., the no. of mols. of reagent used and the viscosity of the resulting soln. as compared with pure C_6H_6 taken as 1: $PhNO$ 0.01, 3.2; 3.0, 1.4. NO_2 0.01, 2.1; 0.05, 1.9; 0.1-1, product pptd. out. Bz_2O_2 0.01, 3.6; 0.5, 2.9. $PhNO_2$ 0.1, 3.7; 1, 3.7. Rubber soln. alone 3.6. If I, then, is not a deriv. of rubber itself but of oxidative degradation products, it should contain somewhat more O than that calcd. for pure isorubber-nitrone, and such is the case. In P. and G.'s published analyses only 2 show C values equal to the theoretical, the other 5 being 1-1.5% too low. S. and J. in about 20 analyses obtained values 1.5-2% too low although they completely excluded air in the prepn. of the I and carried out the filtration and washing in a N atm. As to the mol. wt. of the product, a series of detns. in 1% C_6H_6 soln. gave values about twice as large as in $PhNO_2$, but the latter, which on the av. were only slightly higher than P. and G.'s, varied considerably. I is not a homogeneous substance but a mixt. of polymer-homologous products which can be sepd. by means of cold C_6H_6 into more easily and less easily sol. portions of approx. the same compn. but with different mol. wts. in $PhNO_2$, and forming $CHCl_3$ solns. of different viscosities. Furthermore, it was shown by isothermal distn. in Signer's app. (*C. A.* 24, 4433) that in equally concd. solns. of the 2 portions there are fewer mols. in the soln. of the less sol. portion. The reaction with $PhNO$ does not permit of detg. whether the mol. of rubber is made up of 100 or 1000 isoprene residues. **XXIII. Cryoscopic measurements on rubber solutions.** H. STAUDINGER AND H. F. BONDY. *Ibid* 2900-5.—Reply to Pummerer, Andriessen and Gündel (*C. A.* 24, 1102). Mol.-wt. detns. on rubber in camphor cannot serve to clear up the structure of rubber, for, as already shown, the rubber undergoes extensive degradation to hemi-colloidal cleavage products when heated in molten camphor (170-80°). The ratio of the time of flow of a C_6H_6 soln. of rubber which has been dissolved in molten camphor to the time of flow of a soln. prepd. from the same quantities of rubber and camphor without heating is about 1:15; the rubber recovered from the former soln. has the properties of a deeply degraded hemi-colloidal rubber, is smeary, has almost completely lost its viscosity, dissolves without swelling and forms solns. of low viscosity. The relative viscosities of a 0.2 *M* soln. of pure rubber in tetralin are 14.89 and 2.60, resp., before and after the rubber has been heated with camphor. The sepn. of mixed phases observed by P. and Andriessen in attempts to det. the mol. wt. of rubber in freezing C_6H_6 is easily explained by the fact that concd. rubber solns. in C_6H_6 (1%) are not sol but gel solns.; for rubber purified according to P. the limiting concn., *i. e.*, the transition from sol to gel soln., is about 0.5%, and it is only in the dil. sol solns. that mol.-wt. detns. can be made successfully. With the hemi-colloidal degradation products, mol.-wt. detns. can be made by the f.-p. method;

the limiting concn. of a degraded rubber of polymerization degree 100 is reached in an approx. 5% soln. P. and Gündel express the opinion that S.'s rubber was not completely N-free, but S. and B. were unable to detect any N by heating with K, although a control showed that 0.01% N can be detected in this way. C. A. R.

Swelling pressure of rubber. PAUL STAMBERGER. *Nature* 127, 274(1931); cf. C. A. 24, 4659.—The formula $P = K/V^2$ gives satisfactory results with the data of the previous paper, where P is the swelling pressure, V is the vol. of solvent bound to a unit wt. of jelly, and K is a const. whose meaning is expressed by substituting the above equation in the max. work term: $dA = PdV$. The swelling pressure results from the attraction of solvent mols. by the mols. of the gel. ARTHUR FLEISCHER

The action of lead selenide in rubber mixtures. R. DITMAR AND K. H. PREUSSE. *Caoutchouc & gutta-percha* 28, 15448-50(1931).—Recent interest in Se in the rubber industry led to a study of its derivs. as possible valuable compounding ingredients. The present paper continues the previous work on Se red (cf. C. A. 24, 4663; D. and Preusse, C. A. 24, 4659). Zn selenosulfide (5% Se) and K_2SeSO_3 had no notable effect in rubber mixts., either on the rate of vulcanization or otherwise, so PbSe was next examd. A finely ground natural product (hardness 2.5-3, d. 8.2-8.8) was used. In rubber-S mixts., PbSe has no influence on the rate of vulcanization nor any reinforcing effect. On the mixing mill, PbSe has a strong plasticizing action which becomes marked with 4% PbSe, and accordingly this property may be utilized in prep. adhesive cements from rubber. In the mixt.: crepe 100, S 3, PbSe 2, accelerator 2, whiting 30, the PbSe acts as a very powerful activator with the majority of com. accelerators (the results with 16 are tabulated), so that no other activator is needed, and it also reinforces the vulcanizates, particularly in increasing their resistance to abrasion. Its action, therefore, resembles that of Se. On increasing the PbSe in an accelerated mixt. to 100 parts on the rubber, the reinforcement increased continuously. In cures with S_2Cl_2 in CS_2 or with S_2Cl_2 vapor, PbSe had no action at all, except that because of its softening action (*loc. cit.*) the cure had to be prolonged. C. C. DAVIS

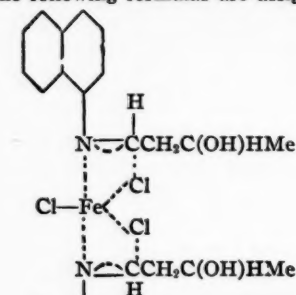
Liquid rubber and carpets. WEBSTER NORRIS. *India Rubber World* 83, No. 6, 56(1931).—An illustrated description is given of the application of rubber dispersions in a new type of carpet. C. C. DAVIS

The curing of sheet rubber. T. E. H. O'BRIEN. *Trop. Agr. (Ceylon)* 75, 280-92 (1930).—Smoking of sheet rubber prevents undesirable surface stickiness. Unsmoked sheet contg. *p*-nitrophenol is inferior in aging properties to a like sample without *p*-nitrophenol. Smoked sheet after vulcanization is superior in aging properties to unsmoked sheet when both contain *p*-nitrophenol. A sheet weighing 1.5 lb. and measuring 23×18 in. is of correct thickness for efficient drying, combined with good appearance, and is also the most suitable size for packing in a standard rubber chest. J. O. H.

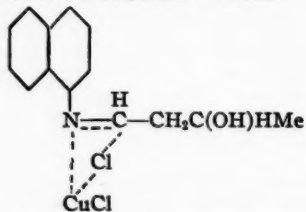
The consistency of the particles in balata latex. E. A. HAUSER. *Kautschuk* 7, 2-3(1931); *Gummi-Ztg.* 45, 1030(1931).—The expts. deal with balata latex from Peru, which was preserved with AcOH. For this reason the acid character of the latex may have brought about certain changes in the consistency of the particles, so that the conclusions drawn from the expts. do not necessarily hold good for the particles of fresh latex. The micromanipulator examn. was carried out with the aid of a new kind of dark-field condenser, with the finest microneedle which was equipped with a new device for its control (cf. C. A. 25, 1409). The examn. shows that there are 2 kinds of particles in such latex: (1) a uniformly tacky kind, which probably represents the resinous components of the latex, and (2) a smaller kind of particle which does not have a homogeneous structure. This 2nd type consists of a viscous inner part and a plastic outer part, which even has a certain degree of elasticity. By evapn. of the latex or by addn. of coagulating agents the consistency of the 1st type changes only slightly or not at all, whereas the 2nd kind of particle contracts to a homogeneous mass. The 2nd kind of particle probably therefore represents the actual balata hydrocarbon. Further expts. proved that during the evapn. only the particles of the 1st type fuse together, whereas the particles of the 2nd type remain distinctly sepd. from each other. This latter fact probably depends upon each hydrocarbon particle having an adsorbed skin of the non-balata components dissolved in the serum. This observation is of particular interest, since it offers the possibility of obtaining pure balata by some convenient method, such as fractional pptn. or fractional sepn. from the latex, without having to resort to extrn. C. C. DAVIS

The protective action of some antioxidants. II. The metal halide compounds of some protective agents against aging, with special reference to aldol- α -naphthylamine. F. KIRCHHOF. *Kautschuk* 7, 7-12(1931); cf. C. A. 23, 3371.—It has already been shown that alc. solns. of heavy metal chlorides change the color of alc. solns. of certain antioxidants like aldol- α -naphthylamine (I), "Stabilite Alba" (II) and "Agerite

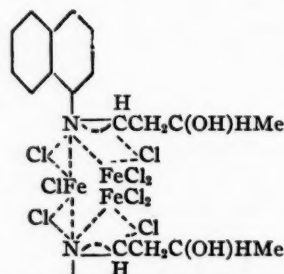
powder" (III), both when viewed in visible and in ultra-violet light. The present paper, in which the behavior of I in particular was studied, attempts to explain this phenomenon, which is of importance not only from the antioxidant point of view, but because of the discoloration of vulcanizates contg. such antioxidants. With AuCl_3 , CuCl_2 , FeCl_3 and PtCl_4 , I gives cherry-red colors at low concns. and intense blue colors at higher concns. of the metal chlorides. The blue colors are, however, unstable and change to violet, then to cherry-red. With AlCl_3 , AsCl_3 , CoCl_2 , FeCl_2 , HgCl_2 , MnCl_2 , NiCl_2 , SbCl_3 , SnCl_2 , SnCl_4 , TiCl_3 , UO_2Cl_2 and ZnCl_2 no colors are obtained. While AuCl_3 , CuCl_2 , FeCl_3 and PtCl_4 cause the disappearance of the fluorescence of I in ultra-violet light, SbCl_3 is the only other chloride of those above which affects the fluorescence, and this gives a yellow-white ppt. From the cherry-red I solns. with CuCl_2 and FeCl_3 , chocolate and coffee-brown *ppts.* with high Cu and Fe contents sep. on long standing, and these remain dark even after long washing with EtOH . Their C_6H_6 solns. are intense yellow-brown. Analysis of the *ppts.* showed that the Cu *ppts.*, which vary from coffee-brown to ochre-yellow, are adsorption compds. of the cherry-red sol. Cu-I compds. with solid I, and that the Fe *ppts.*, which are chocolate-brown, are adsorption compds. of the sol. cherry-red Fe-I compds. with solid I. These reactions are not the same as that of aq. I with aq. FeCl_3 , ZnCl_2 , AgNO_3 and CrO_3 (cf. "Meyer-Jacobson," II, 350), because water and dil. alkalis cause cleavage of the alc. Cu and Fe compds., with formation of blue-violet flocculant *ppts.* which contain no metal and which become yellow-brown in air. Since these color reactions are confined to chlorides of a higher state of oxidation, the more loosely combined halogen plays the essential part. The fact that the reaction with CuCl_2 is in every case more rapid than with FeCl_3 , may be utilized to distinguish analytically small quantities of these compds. A similar color reaction occurs with free halogen, *e. g.*, Br in CCl_4 , where a deep indigo appears immediately, changes to violet, then to cherry-red and finally to yellow-brown. These Br addn. compds. give no color reaction with FeCl_3 or CuCl_2 , so that in the color reaction the metal halide combines at the double bond between the N and CH. Since the cherry-red I- FeCl_3 and I- CuCl_2 compds. are decompd. by small quantities of HCl to yellow-brown products, only unstable compds. are formed, and since the quantity of addn. compd. depends upon the concn. of halide, the N does not always have the same valence, and the following formulas are assigned:



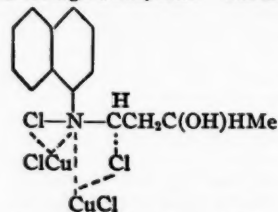
Cherry-red soln. (3-valence N)
from low FeCl_3 concn. Stable



Cherry-red soln. (3-valence N)
Stable



Blue-violet soln. (4-valence N)
from high FeCl_3 soln. Unstable



Blue soln. (4-valence N)
Unstable

These resemble the hemin (IV) formula of Willstätter and Küster. The I-metal halide solns. absorb all visible light up to a bright band in the red and orange between 560 and 680 μ , and since HCl solns. of IV show a similar band, the absorption limits may be characteristic of the FeCl₃ and CuCl₂ groups. The ultra-violet fluorescence of all the I-metal halide compds. is very feeble compared with that of the original substance, and the colors vary greatly. The following fluorescent colors appeared in EtOH in ultra-violet light: I, intense sky-blue; I + FeCl₃, very pale violet; I + CuCl₂, pale yellow-green; I + CuCl₂ + HCl, pale green-brown; I + Br, pale violet; II intense violet; II + CuCl₂, pale yellow-green; II + CuCl₂, pale yellow-green; II + CuCl₂ + HCl, pale green-brown; II + Br, pale brown; IV + alc. HCl, pale red-brown. The source of the strong fluorescence is probably in the N—CH double bond, and it is lost by addn. of the halide. The O-transporting power of Fe in hemin occurs also in the I-metal halide and II-metal halide compds., for I soln. made pale rose by FeCl₃ becomes deep blood-red when O is passed through it, whereas I soln. alone is pale yellow. The O-transporting power of the CuCl₂ compds. is many times greater than that of the corresponding Fe compds. and this agrees with the similar behavior of Fe and Cu compds. in rubber. With 1% CuCl₂, O caused a turbidity with I and intense carmine with II, by the formation of oxidation products, and after prolonged passage of O, about 50% of the dissolved substances sepd. as a chocolate-brown ppt. contg. only a small percentage of combined Cu. Treatment of I soln. contg. FeCl₃ for many hrs. gave an intense carmine color, with no insol. oxidation products. Not only is the auto-oxidation of antioxidants greatly accelerated by their FeCl₃ complexes and especially by their CuCl₂ complexes, but it is inhibited by catalytic poisons. Thus with II-CuCl₂ soln., a little HCN greatly retards the time of appearance and the intensity of the carmine which is formed upon treatment with O. III gives no immediate color with alc. FeCl₃ or CuCl₂, but on long standing in air a brown color appeared, because of oxidation. III is probably more stable than I and II toward oxidizing agents and oxidation catalysts. In titrating III in ultra-violet light, the quantity of FeCl₃ required to destroy the violet fluorescence is approx. 2 mols. of FeCl₃ per mol. of III. II gives no immediate color with FeCl₃, but on long standing a carmine color appears, especially in light. II and CuCl₂ give an immediate yellow or yellow-brown which changes soon to deep carmine. The carmine solns. with II and FeCl₃ and CuCl₂ show similar spectral properties, and are not changed by HCl, in contrast to the colors with I complexes. In titrating in ultra-violet light, only 0.5 mol. of FeCl₃ or CuCl₂ is required to destroy the fluorescence of the II-FeCl₃ and II-CuCl₂ complexes. Based on the similar absorption spectra of these metal halide complexes with the previous ones, they probably contain similar FeCl₃ and CuCl₂ complexes which cause the colors. The Fe complex

would be PhN₂CH₂CH₂NPh₂FeCl, where the stability toward HCl results from the formation of high valences. Since antioxidants are oxidized in time by autooxidation they protect an antioxidantizable substance like rubber only as long as they remain active. Since traces of sol. heavy metal compds., especially of Fe, are invariably present in rubber compounding ingredients, rubber mixts. which contain protective agents are discolored by the formation of dark colored metal complexes and their oxidation products.

C. C. DAVIS

Gathering, treatment and properties of guttapercha. H. R. BRAAK. *Chem. Weekblad* 27, 567-71(1930).—A review.

A. L. HENNE

Age-resistant rubber. A survey of United States and foreign patents for chemical prevention of the deterioration of rubber. JOSEPH ROSSMAN. *India Rubber World* 83, No. 5, 65-8(1931).

C. C. DAVIS

New light on vulcanization. The process as revealed by electrical tests. W. H. NUTTALL and J. KIRKWOOD. *India Rubber J.* 80, 657-60(1930).—A review and discussion, with particular reference to the work of Curtis, McPherson and Scott (*C. A.* 22, 330), Kitchen (*C. A.* 23, 2375) and Boggs and Blake (*C. A.* 24, 4425). C. C. D.

Tensile tests of vulcanized rubber at high speed. A. VAN ROSSEM and H. B. BEVERDAM. *Rev. gén. caoutchouc* 7, No. 57, 27-34(1930).—Most of the testing machines used for detg. the elongation of rubber have a slow speed, and 60 cm. per min. is somewhere near the speed usual in practice, regardless of the state of cure. This is in spite of the fact that undervulcanized rubber, which has a high elongation when stretched at slow speed, is brittle when stretched very rapidly, and has an extremely low elongation. For this reason, it was of interest to make elongation tests at high speeds. No app. was available for recording the stress-strain curve, and resort was had to the pendulum app. of Charpy. The technic employed in adapting this app. to the present expts. is described and illustrated. Different accelerated rubber mixts. at various states of cure were tested in this way. The energy at rupture was calcd.

and the results were compared with tests on the Schopper dynamometer. The results show that (1) the max. energy at rupture as a function of the time of vulcanization is much more sharply defined at the high speeds of the pendulum app. than in the tests with the Schopper machine, and (2) the max. strength with the pendulum app. is at a lower state of cure than with the Schopper machine. With vulcanizates contg. a low percentage of S, e. g., the mixt.: rubber 100, S 3, diphenylguanidine 1, ZnO 5, the pendulum app. gives a less sharply defined max., but nevertheless here too this max. is at a lower state of cure than that with the Schopper machine. The influence of loading with pigments and fillers was also studied. The magnitude of the max. depends upon the substance added, but the sharpness of this max. and its relation to the time of vulcanization are independent of the nature of the filler. Accelerated aging tests were made in the Geer oven at 70° and the aged vulcanizates were then tested in the same way. After aging, the time of cure/energy at rupture curve obtained from the Schopper machine was similar to that obtained from the pendulum app. before heating. The energy at rupture curve detd. by the pendulum app. is therefore of great importance in relation to the state of cure, because the time of vulcanization which corresponds to the max. energy at rupture by the pendulum app. is, contrary to the time of vulcanization corresponding to the max. tensile strength by the Schopper dynamometer, the time of vulcanization which corresponds to the best aging. The importance of tests at the high speeds and the shortcomings of the pendulum app. for this purpose make it desirable that an app. be developed which at a very rapid speed of stretching will: (1) det. the resistance to stress, the ultimate elongation and the energy at rupture; (2) record graphically the relation between the stress and the elongation and (3) perform at different speeds. Also in *Kautschuk* 6, 224-9(1930). C. C. DAVIS

Hard spots in vulcanized rubber compounds. J. H. HOWEY. *Ind. Eng. Chem.* 23, 287-90(1931).—Expts. are described, the object of which was to ascertain the cause of local variations in the hardness of exptl. slabs of rubber mixts. of the C black tread type. It was found that areas of excessive hardness correspond to regions where the max. flow or displacement occurs when the rubber mixt. is pressed into the mold at the time of curing. A knowledge of this fact is of importance in testing the hardness of a vulcanizate by the Am. Soc. of Testing Materials standard of hardness, and for increasing the precision and reliability of this convenient test. It was also found by chem. analysis that these variations in hardness cannot be attributed to heterogeneous regions (non-uniform compn.) in the rubber-S-accelerator-pigment mixt., and it is concluded that the variations must depend either upon altered conditions of dispersion in the regions of max. displacement or else upon a local grain effect set up by the flow. C. C. DAVIS

The plasticizing of rubber. F. JACOBS. *Rev. gén. caoutchouc* 8, No. 69, 17-27 (1931); cf. C. A. 25, 1705.—A review and discussion of the properties of gutta resins, various pine products and fatty acids. C. C. DAVIS

Hard rubber—its main applications. T. R. DAWSON. *The Times Trade and Eng. Suppl.* 28, No. 664, 18(1931). E. M. SYMMES

Organic rubber colors. F. HARRIS COTTON. *India Rubber J.* 81, 413-4(1931); cf. C. A. 25, 1117.—A general discussion, with 21 references. C. C. DAVIS

Stretch in rubber transmission belting. C. W. STAACKE. *Proc. Am. Soc. Testing Materials* 30, Pt. II, 944-56(1930).—The expts. were made to det. the proper inelastic stretch to remove from belting contg. a given fabric during the vulcanization process. C. C. DAVIS

A study of the performance characteristics of a 4-inch 4-ply rubber transmission belt. J. E. SKANE. *Proc. Am. Soc. Testing Materials* 30, Pt. II, 928-43(1930).—The tests were made to det. the performance of the belt under varying loads, speeds and slips. C. C. DAVIS

Substitutes for natural rubber—difficulties of synthetic process. HENRY P. STEVENS. *The Times Trade and Eng. Suppl.* 28, No. 664, 26(1931).—A review. E. M. SYMMES

Synthetic rubber. ERNST KLEIBER. *Kunststoffe* 20, 5-6(1930).—A review. B. H.

Evaluating gas blacks by the D. P. G. [diphenylguanidine] adsorption method. I. DROGIN. *India Rubber World* 83, No. 6, 57-9, 62(1931).—Not all gas blacks adsorb a given accelerator to the same extent, and therefore the rate of vulcanization of a rubber mixt. contg. the accelerator varies with the gas black used. The analytical method described is claimed to be reliable in evaluating the effect of gas blacks on the rate of vulcanization and on the phys. properties of the vulcanizate, with diphenylguanidine as accelerator. *Procedure.*—Agitate 2 g. of gas black with 100 cc. of MeOH solns. of diphenylguanidine of 6 different normalities (0.0025-0.20 N), centrifuge and titrate

10 cc. of the supernatant liquid with MeOH solns. of HCl of the corresponding normalities (bromophenol as indicator). All calcns. are expressed volumetrically in terms of a single normality of HCl. The quantity of diphenylguanidine adsorbed as a function of the quantity remaining in soln. (both in terms of HCl), when expressed in graphical form (ordinate and abscissa, resp.) gives a curve which, converted to a logarithmic basis, becomes a straight line. The distance between the abscissa axis and the point of intersection of this straight line with the ordinate axis represents the logarithm of a const. The antilogarithm of this const. represents the value of the gas black. Exptl. data show the application of this method to 4 different gas blacks. C. C. DAVIS

Behavior of various clays with crude and reclaimed rubber. H. A. WINKELMANN AND E. G. CROAKMAN. *Ind. Eng. Chem.* 22, 865-9(1930).—Often the influence of 2 different clays on the properties of a rubber mixt. is greater in the uncured than in the cured mixt. The present paper shows the variations in raw rubber and in reclaimed rubber produced by various com. clays, as judged by plasticity, retentivity, phys. tests, artificial aging and chem. analysis. A microscopic examn. also shows the relation between particle size and phys. properties of the raw and reclaimed rubbers. The results are described in detail and shown graphically, and lead to certain general conclusions: (1) Chem. analysis of a clay gives little or no useful information about its behavior in raw or reclaimed rubber. On the other hand, its acidity or alkali has an influence on the rate of vulcanization and should be detd. The color of a clay does not indicate its purity or behavior. (2) There are wide differences in the effects of different clays on the plasticity, retentivity and softness of raw and reclaimed rubbers. (3) In cured new and reclaimed rubbers, clays vary greatly in their effect on the phys. properties, the same relative effects being obtained in the new and reclaimed rubber mixts. There is not, however, so much variation in tensile strength in reclaimed rubber vulcanizates as in new rubber vulcanizates. (4) Artificial aging in compressed O serves better to distinguish clays and is an important test in judging their merits. (5) By microscopic examn. it is possible to judge the relative effects of clays in new and reclaimed rubber, both uncured and cured. C. C. DAVIS

Rosin and rosin oil in rubber and reclaimed rubber. H. A. WINKELMANN AND E. B. BUSENBURG. *Proc. Am. Soc. Testing Materials* 30, Pt. II, 807-27(1930).—Rosin and rosin oil can be satisfactorily used as softeners for rubber, with due regard to proper compounding conditions. Different types and grades of rosin and rosin oil are described, and the phys. properties of both gum and wood rosins are given in tables. "Synthetic" rosin oils of low rosin content, retort pine tar and kiln pine tar, having acid nos. of 65-90, can be used interchangeably as softeners, but rosin oils contg. much rosin, rosin itself or neutral rosin oil must each be handled differently. Besides acting as a softener during the mfg. process, rosin also activates the accelerators, but because of its relatively greater effect as a softener the cure is slower with rosin than with fatty acids. To prevent rosin from lowering the modulus and tensile strength of rubber, greater proportions of accelerator must be used. Three different grades of rosin appeared to affect modulus, tensile strength and aging equally. If wood rosin is substituted for the pine tar in an ordinary tread stock formula, the rate of vulcanization and tensile strength are slightly lowered, and if substituted for the stearic acid there is considerable softening and the rate of vulcanization is lowered. A no. of expts. are described, in which various grades of gum and wood rosin, pine tar and "synthetic" rosin oil are incorporated as softeners in a rubber compn. and their effect on plasticity, "nerve," elongation and tensile strength, aging and softness ascertained. Rosin is also useful in imparting tackiness to rubber, and as a devulcanizing agent. Also in *India Rubber World* 83, No. 6, 63-5, 67(1931); 84, No. 1, 56-8(1931). H. K. SALZBERG

Some recent engineering applications of rubber. J. R. HOOVER AND F. L. HAUSHALTER. *Ind. Eng. Chem.* 23, 462-9(1931).—The discussion includes rubber bearings, electrodeposited rubber products, absorption of vibration and noise, heat-resisting and oil-resisting rubber products, rubber products resistant to chemicals, rubber as a preventive of aviation ice hazard and various other applications. C. C. DAVIS

Toxic substances in the rubber industry. XX. Sulfur monochloride. P. A. DAVIS. *Rubber Age* (N. Y.) 29, 77-8(1931); cf. C. A. 25, 2329.—A review and discussion of the physiol. properties of S_2Cl_2 and preventive and remedial measures to be taken. C. C. DAVIS

Accelerated discoloration tests for white rubber products and methods of measuring the extent of the discoloration. HARLAN A. DEPEW. *Rubber Age* (N. Y.) 29, 27-30(1931).—The discoloration (yellowing) of vulcanized rubber upon exposure to sunlight is a function of (1) the character of the light (the shorter the wave length the more rapid the discoloration); (2) the temp. (the higher the temp. the greater the discoloration) and probably (3) moisture (the yellow color is leached away by water).

Light from a Hg arc may be used as the basis of an artificial discoloration test, and the changes in color may be measured by a "K. and E." color analyzer. In this way it was shown that the higher the lithopone content of vulcanized rubber the less did the latter discolor, and that ZnO inhibited the yellowing of vulcanizates contg. lithopone.

C. C. DAVIS

The effect of grit upon the stress and strain properties of a carbon-black stock. E. P. W. KEARSLEY AND C. R. PARK. *Rubber Age* (N. Y.) 29, 79-80(1931).—From a practical point of view, a small proportion of grit in C black does not impair the resistance to abrasion of a vulcanizate contg. it, as shown by Twiss (cf. C. A. 20, 3838), and it is only the ultimate elongation and tensile strength which may be seriously affected. The present paper describes expts. on this latter effect, a field of investigation not well covered in the literature. To the base mixt.: rubber 100, S 3.5, diphenylguanidine 1.25, ZnO 5, were added samples of a C black to which had been added increasing proportions of C-black grit from elsewhere. The mixts. were cured 20, 60 and 90 min. at 140° and tested for tensile strength and modulus. Up to 3% the grit had no measurable effect on the tensile strength or on the modulus. Above this proportion, the values began to decrease progressively. When poor results are obtained with gas black, factors other than grit are responsible, notably poor dispersion of the pigment (cf. Endres, C. A. 19, 1208). Agglomerates in the unwet state disintegrate upon stretching and form points of weakness. The present-day tendency to minimize times of mixing results in incomplete dispersion, and it is probable that premature tread wear and cracking are a result of this rather than of gritty pigments.

C. C. DAVIS

A contribution to the problem of the impregnability of cord threads with rubber. E. A. HAUSER AND M. HÜNEMÖRDER. *Metallgesellschaft Periodic Rev.* No. 5, 13-8 (1931).—There is almost no literature on the impregnability of fabrics by latex and by rubber in org. solvents except the investigations of Dieterich (C. A. 24, 1543) and Grenquist (C. A. 22, 4875), and the methods used by both give untrustworthy results because of the changes which may take place during the rigorous treatment. For this reason a new microscopic method was developed which should be free of these shortcomings and with which were examd. fabric or cord (1) covered with visibly thick rubber, e. g., coated on both sides with or without previous impregnation, and (2) protected by a rubber coating of no significant thickness, e. g., impregnated with latex or rubber in an org. solvent. In case (1) the sample is set in hard paraffin, dissected and frozen with CO₂ to a depth of 200 μ ; a microsection 20-30 μ thick is cut on a sliding microtome, immersed in warm water, dried on a microscope slide, immersed in concd. H₂SO₄ for 1-2 hrs., washed clean with H₂SO₄ and examd. directly or preserved in Canada balsam. In case (2) the sample is immersed in 7% gelatin soln. and solidified by cooling, and the same procedure used as before. The samples thus examd. were: (1) thread soaked in 5% benzene rubber soln.; (2) sample (1) after treatment with H₂SO₄; (3) thread soaked in 33% latex (ammoniated); (4) sample (3) after treatment with H₂SO₄; (5) dry cord threads frictioned with rubber; (6) sample (5) after treatment with H₂SO₄; (7) cord fabric soaked in rubber in C₆H₆, then skimcoated on both sides and finally treated with H₂SO₄; (8) latex cord fabric coated on both sides and treated with H₂SO₄; (9) cord fabric coated on both sides and after vulcanization treated with H₂SO₄; (10) latex cord fabric coated on both sides and after vulcanization treated with H₂SO₄; and (11) dry cord fabric in sheets treated with H₂SO₄ after vulcanization. Microscopic examn. of these different samples made possible, in conjunction with earlier expts. on phenomena taking place during vulcanization (cf. C. A. 22, 4876; 23, 3597), the drawing of certain general conclusions. A fabric previously soaked in a C₆H₆ soln. of rubber is already completely impregnated with rubber before vulcanization, whereas a fabric soaked in latex is only covered with an external coating of rubber, even after vulcanization. When threads which have not been treated are embedded in rubber sheets, or when rubber mixts. are frictioned on dry fabrics, there is no impregnation previous to vulcanization, but impregnation takes place to a high degree during vulcanization as a result of the flow of the rubber. The extent to which weftless cords can be impregnated in a vulcanized state depends not upon whether the fabric has been previously treated but upon the phys. condition of the rubber. The reason that the rubber in latex is merely deposited on the surface is that the rubber hydrocarbon is present as particles whose av. diam. is 1-2 μ , and the capillary interstices of the fibers are smaller than these particles. The question whether cord fabrics and weftless cords prepd. with C₆H₆ solns. of rubber or those with latex are superior in strength, elasticity and durability is not settled by the present investigation.

C. C. DAVIS

Graphical tensile-testing machine for rubber threads. S. H. HAHN AND E. O. DIETERICH. *Ind. Eng. Chem., Anal. Ed.* 3, 218-21(1931).—The new machine, the construction and operation of which are described in detail, allows the testing of threads

having breaking strengths of approx. 400-2000 g. and elongations up to 1000%, with great precision at 200-700% elongation. Curves show the stress-strain curves of typical threads by this method, and a comparison in 1 case with the stress-strain curve of the same vulcanizate by the ordinary method.

C. C. DAVIS

Experiments on some technical mixtures with reference to their electrical properties. F. JACOBS. *Kautschuk* 7, 4-7(1931).—The object of the expts. was to ascertain to what extent the compn. and the color of rubber matting influence the elec. insulating power. In expts. already described (cf. *C. A.* 24, 4658) it was found that certain coloring agents like ochre and C black have unfavorable effects on the resistance to elec. puncture. In places where the sheets were united during vulcanization, and at the junctions of 2 colors in mottled samples, the resistance to breakdown was no lower than in the corresponding homogeneous sections. The higher the voltage the shorter the time before breakdown. A systematic study of the influence of various fillers on the dielec. resistance of matting was carried out by using a base mixt. contg. 45% natural whiting and comparing the behavior of this with corresponding mixts. contg. kaolin, kieselguhr, slate, powd. marble and pptd. CaCO_3 instead of whiting. With kaolin and with pptd. CaCO_3 the resistance to elec. breakdown was less than with the other fillers. Kieselguhr and powd. marble gave the highest resistances, followed by slate and natural whiting, which were greatly inferior to kieselguhr and powd. marble. In every case the green matting samples contg. Cr_2O_3 were inferior to the gray ones. The quant. results of the elec. measurements are given in tables.

C. C. DAVIS

Accelerators of vulcanization. F. JACOBS. *Caoutchouc & gutta-percha* 28, 15438-45 (1931); cf. *C. A.* 25, 2330.—The manuf., phys. and chem. properties and behavior from an accelerating point of view of com. thiuram derivs. are described, with quant. data. *Ibid* 15485-91.—The properties and behavior of tetramethylthiuram disulfide under various conditions and in various types of rubber products are described, with quant. data.

C. C. DAVIS

Patents

Rubber. I. G. FARBERIND. A.-G. Fr. 689,128, Jan. 30, 1929. The aging of natural or artificial rubber is prevented by adding indanphenols which have, *e. g.*, the formula $\text{C}_6\text{H}_4\text{.CH}_2\text{.CH}_2\text{.CHR}$, in which R is an aromatic group substituted by at least

one OH group, and all the groups may contain univalent substituents (cf., *e. g.*, Fr. 636,606).

Rubber. I. G. FARBERIND. A.-G. Fr. 690,043, Feb. 15, 1930. Lampblack is introduced into rubber or the polymerization products prepd. from butadiene hydrocarbons or their derivs., by making a mixt. of lampblack and a liquid product obtained by incomplete polymerization of a hydrocarbon or hydrocarbon deriv. and incorporating the mixt. with the rubber, etc.

Rubber. I. G. FARBERIND. A.-G. Fr. 690,453, Feb. 22, 1930. Tars obtained from the controlled carbonization of lignites, etc., and deprived of their volatile fractions by distn. are used as fillers for natural or synthetic rubber instead of lampblack. The residue from the distn. may be extd. with acetone or other compds. before use.

Rubber from latex. ALFRED ZANGGER. Fr. 689,424, Feb. 4, 1930. Rubber is extd. from latex of plants growing in the temperate zone and trees other than those called rubber trees by the action of CCl_4 .

Rubber deposition by electrophoresis, etc. DUNLOP RUBBER CO., LTD., R. G. JAMES and D. F. TWISS. Brit. 334,581, June 6, 1929. In the electrophoretic deposition of materials such as rubber from a dispersion the particles of which normally carry a neg. charge, the H-ion concn. is increased in the presence of formaldehyde to effect reversal of the charge on the particles without causing coagulation; deposition is then effected on the cathode or a porous or semipermeable mold surrounding it. Various details, examples and modifications of procedure are described.

Electrophoretic deposition of rubber. THE ANODE RUBBER CO., LTD. Ger. 512,170, Sept. 5, 1925. This corresponds to Brit. 257,885 (*C. A.* 21, 3141), but gives specific examples.

Treating rubber. DEUTSCHE HYDRIERWERKE A.-G. Fr. 689,541, Feb. 7, 1930. Alcs. of high mol. wt. such as dodecyl or octadecyl alcs. are used as accelerators or protectors against aging in the treatment of rubber.

Preserving rubber from aging. ALBERT M. CLIFFORD (to Goodyear Tire & Rubber

Co.). U. S. 1,788,860, Jan. 13. Small proportions of substances such as α -amino- β -naphthol or α -chloro- β -naphthol (suitably about 1%) are added to rubber compns.

Preserving rubber against aging. WM. D. WOLFE (to Goodyear Tire & Rubber Co.). U. S. 1,788,903, Jan. 13. Amino-*p*-hydroxydiphenyl (suitably about 1%) is used as an antioxidant or age-retarder, and may be prepd. (by a process details of which are given) from *p*-hydroxydiphenyl by nitration and subsequent reduction.

Rubber compositions. JACQUES DELPECH. Fr. 689,445, Feb. 5, 1930. Rubber is made non-slippy by the addn. of powd. leather, cotton, wool, etc.

Rubber composition with linseed oil. EUGENE E. AYRES, JR. (to B. A. S. Co.). U. S. 1,789,062, Jan. 13. An aq. dispersion of rubber is emulsified with linseed oil, heated with agitation, and air is blown through the material. A product is thus obtained which is suitable for waterproofing, elec. insulation, floor covering, paint and varnish manuf., etc.

Coloring rubber. IMPERIAL CHEMICAL INDUSTRIES, LTD., A. J. HAILWOOD, W. J. S. NAUNTON, A. STEWART and A. SHEPHERDSON. Brit. 334,688, Aug. 15, 1929. The pigments used for coloring rubber as described in Brit. 304,376 (C. A. 23, 4848) are prepd. by coating the filler with the vat dye by oxidizing an alk. soln. or suspension of the leuco compd. of the vat dye in the presence of the filler (such as $MgCO_3$), the latter being treated (before or after incorporation of the dye) with a soap. The use of soap produces pigments giving brighter shades than those prepd. without soap.

Recovery of rubber. CAOUTCHOUC RÉCUPÉRÉ RÉNO. Fr. 689,904, April 22, 1929. Rubber and textile fibers in used tires, etc., are sepd. and recovered in 2 stages: in the first the waste rubber is soaked and made to swell by oil obtained by the dry distn. of waste rubber, and in the 2nd the textiles and rubber are sepd. by mech. operations. The rubber is preferably regenerated by treatment with NaOH.

Rubber articles. SOCIETÀ ITALIANA PIRELLI and UGO PESTALOZZA. Fr. 36,738, Mar. 5, 1929. Addn. to 651,684 (C. A. 23, 3599). In making rubber articles by local heating according to Fr. 651,684, a di-substituted aromatic compd. of guanidine such as *sym*-diphenylguanidine, *sym*-phenyl-*o*-tolylguanidine or *sym*-di-*o*-tolylguanidine is added to the latex before heating.

Apparatus for "plasticating" rubber (comprising feeding screws and an extrusion nozzle, etc.). W. A. GORDON (to Farrell-Birmingham Co.). Brit. 334,509, April 23, 1929. Structural features.

Covering fabric with rubber. V. D. OTSING. Russ. 34,708, Nov. 1, 1928. The fabric is first impregnated with a sol. Mg salt and then treated with NH_4OH to ppt. MgO on the fabric. The dried fabric is treated with rubber by the usual methods.

Cords for use in vehicle tire manufacture. WALLACE H. PAULL and REGINALD TRUESDALE (to Dunlop Tire and Rubber Corp. of America). U. S. 1,788,439, Jan. 13. Fibrous ramie and artificial silk are used together.

Corrugated rubber tubing covered with twill of similar material. DUNLOP RUBBER CO., LTD., and F. W. WARREN. Brit. 334,440, Nov. 1, 1929. Various details of manuf. are described.

Paints for rubber tires, shoe soles, etc. W. E. FRITH. Brit. 334,693, Aug. 23, 1929. Celluloid paint mixed with fine sand is applied to provide a non-slipping surface, and to preserve and waterproof the material.

Synthetic rubber. I. G. FARBENIND. A.-G. Brit. 334,184, May 25, 1929; Fr. 688,790, Jan. 24, 1930. A diolefin such as butadiene is polymerized in the presence of alkali or alk. earth metals (such as Na wire or Na dust) and in the presence of a cyclic di-ether such as dioxane or its derivs. to facilitate polymerization (suitably at a temp. of 40-65° in a rotary autoclave). Solvents or diluents such as benzene, gasoline or ether also may be present. Cf. C. A. 25, 845.

Synthetic rubber. I. G. FARBENIND. A.-G. Fr. 689,070, Jan. 29, 1930. Synthetic substances of the nature of rubber are improved by a treatment with org. nitro compds. such as $PhNO_2$, $C_6H_4(NO_2)_2$, dinitronaphthalene and $C_6H_3(NO_2)_3$. Several examples are given, the rubber compd. being heated with the nitro compd. in soln. in an org. solvent.

Synthetic rubber. I. G. FARBENIND. A.-G. Fr. 689,404, Feb. 4, 1930. Synthetic rubber, particularly suitable for vehicle tires, is made by polymerizing mixts. of dimethylbutadiene with other butadiene hydrocarbons such as butadiene or isoprene or a mixt. of butadiene and isoprene.

Synthetic rubber compositions. I. G. FARBENIND. A.-G. Brit. 334,554, June 5, 1929. Finely divided C is added to mixed hydrocarbon-artificial rubber products such as mixts. of polymers of butadiene and of 1,3- or 2,3-dimethylbutadiene, mixts. of "heat" butadiene rubber and "emulsion" butadiene rubber or mixts. of butadiene-Na rubber and isoprene "emulsion" rubber.

Rubber-like mass. GOSUDARSTVENNOYE VSESOYUZNOYE OB'EDINENIE BUMAZH-NOI PROMUISGLENNOSTI. Russ. 11,305, Oct. 11, 1926. Fungi belonging to the types Polyporaceae or Agaricaceae are dried, disintegrated to a fine powder, and agitated with turpentine, acetone, ether and similar org. solvents until a uniform consistency is reached. The mass is passed through rollers or other app. used in the rubber and paper industries and then formed into the desired shape.

Artificial materials. I. G. FARBENIND. A.-G. Fr. 690,484, Feb. 24, 1930. Artificial materials of all sorts are made from derivs. of polymerization products not distillable without decompn. of butadiene hydrocarbons. The derivs. are prepd. by introducing by addn. or substitution, elements or uni- or multi-valent groups. Thus, when butadiene hydrocarbons are polymerized with Na, the Na may be replaced by COOH by treatment with CO_2 . Examples are given.

Artificial materials. I. G. FARBENIND. A.-G. Fr. 691,357, Nov. 21, 1929. Artificial materials are made by heat treatment of the polymerization products of butadiene hydrocarbons in a finely divided state, and in a form capable of being hardened. Other substances capable of being hardened may be added.

Rubber vulcanization accelerator. HOWARD W. MATHESON (to Canadian Electro Products Co.). U. S. 1,788,773, Jan. 13. An accelerator is produced by condensing acetaldehyde and the fractions b. 200–275° from the distn. of a product resulting from the passage of C_2H_2 into aniline at a temp. of 60–120° in the presence of a catalyst such as Cu_2Cl_2 . Cf. C. A. 24, 752.

Composition for use as an accelerator in the vulcanization of rubber. CLAYTON O. NORTH (to Rubber Service Laboratories Co.). U. S. 1,787,258, Dec. 30. A product is formed by combining the reaction product of substantially 3 mol. proportions of butyl aldehyde and 1 mol. proportion of aniline, the reaction product of substantially 3 mol. proportions of AcH and substantially 2 mol. proportions of aniline, creosote oil and pine oil. Cf. C. A. 25, 618.

Vulcanizing agent for rubber. HENRY C. L. DUNKER. Ger. 510,837. Mar. 20, 1928. Se is used as the vulcanizing agent in the manuf. of rubber shoes.

Apparatus for vulcanizing rubber tires. J. FERGUSON & SONS, LTD., and A. S. WELCH. Brit. 334,601, June 7, 1929. Structural features.

Vulcanizing rubber tires, etc. INDUSTRIAL PROCESS CORP. Brit. 334,695, Nov. 26, 1928. In a process for vulcanizing products such as tires in which mixed gases are employed as the heating medium in a gas bag (as described in Brit. 205,577 (C. A. 23, 4756)), the gas bag is brought to a desired temp. before each operation, to ensure uniformity of treatment. Cf. C. A. 24, 4426.

Rubber. THE ANODE RUBBER CO., LTD. Ger. 511,837, Feb. 23, 1927. Aq. dispersions of vulcanized or unvulcanized rubber, regenerated rubber, factice, etc., are obtained by adding a dispersion agent or protective colloid, e. g., olein and NH_3 , during the mech. working up of the rubber, etc., with alkali.

Rubber. FIRMA TOKYO GOMU KABUSHIKI KAISHA. Ger. 512,747, June 4, 1927. A rubber mixt. which floats in water and withstands mineral oil is prepd. by mixing alkali soap with the rubber from factice S and diphenylguanidine. Inorg. filling material is omitted.

Rubber. ISIDOR TRAUBE. Ger. 512,599, July 13, 1926. Latex or latex concentrations are coagulated by addn. of gall or gall-contg. mater. al. Org. solvents such as C_6H_6 , CHCl_3 , oil of turpentine, etc., may be added before or during the addn. of gall.

Rubber. DUNLOP RUBBER CO., LTD., and THE ANODE RUBBER CO., LTD. Fr. 691,556, Mar. 7, 1930. The alkalinity of rubber latex dispersions, which have been preserved by a base such as NH_3 , is reduced by a treatment with absorbent agents belonging to the class which contain SiO_2 -gel, colloidal Al_2O_3 , and active C.

Rubber. SHERARD O. COWPER-COLES. Fr. 691,912, Nov. 15, 1927. Rubber is prepd. by electrolytic deposition from latex on a suitable base as anode in an intermittent manner, either by passing the current at intervals through the latex or by removing at intervals from the action of the current the surface on which the rubber is deposited. NH_4OAc may be added to the latex to increase the cond. Powd. metal may be deposited at the same time as the rubber.

Rubber latex. JACQUES AUMARÉCHAL and GEORGES ROBRIEUX. Fr. 692,076, April 16, 1929. The viscosity of latex is increased by submitting it to a cooking and then pptg. at low temp. the vegetable gelatinous materials without coagulating the globules of rubber by chem. salts having a sp. action on these materials. An example is given using $\text{Pb}(\text{OAc})_2$ as pptg. agent. Fr. 692,077 describes the removal of preservers from latex by converting them into accelerators of vulcanization, by the introduction of chem. compds. capable of uniting with them without coagulating the rubber. Thus, if NH_3 or aromatic amines are used as preservers, aldehydes or CS_2 are

added to convert them to accelerators. Fr. 692,078, May 2, 1929, describes an app. for congc. latex.

Rubber deposition by electrophoresis. SIEMENS & HALSKE A.-G. Brit. 334,871, Jan. 17, 1929. The process for electrophoretic deposition of rubber by a. c. described in Brit. 307,747 (C. A. 24, 265) is modified by the introduction of electrolytes (such as $MgCl_2$, NH_4Cl or $HOAc$) into the latex itself or by satg. the porous molds surrounding the electrodes with electrolytes (instead of or in addn. to the introduction of electrolytes into the electrode spaces). A detailed example is given of the use of electrodes covered with plaster of Paris and satd. with a 20% $CaCl_2$ soln.

Rubber compositions. THE BARRETT CO. Fr. 691,828, Mar. 12, 1930. A softening and dispersing agent for making rubber compositions consists of a tar oil free from cryst. substances at 25°, having a sp. wt. not less than 1.06 at 38° and boiling above 200°. Examples and the properties of the resulting compns. are given.

Preserving aldehyde-amines in rubber batches. SHERMAN I. STRICKHOUSER (to The Dominion Rubber Co., Ltd.). Can. 308,123, Jan. 27, 1931. The deterioration of aldehyde-amine condensation products in rubber batches is retarded by mixing the products with rubber in the presence of hydroquinone.

Antioxidant for rubber. ALBERT M. CLIFFORD (to Goodyear Tire and Rubber Co.). Can. 308,362, Feb. 3, 1931. Rubber is preserved by vulcanizing in the presence of an arylamine deriv. of diaminotriphenylmethane.

Age-resisting rubber. HAROLD W. ELLEY (to E. I. du Pont de Nemours & Co.). Can. 308,347, Feb. 3, 1931. Rubber is made resistant to aging by incorporating the reaction product of α -naphthol and an amine in the mixt. before vulcanization. Cf. C. A. 24, 3925.

Retarding the aging or deterioration of rubber. THE NAUGATUCK CHEMICAL COMPANY. Ger. 512,659, Feb. 8, 1930. The process consists of treating rubber with diaminodiphenylmethane or a CH_3O condensation product. Tables showing the effect of these addns. on rubber after intervals of artificial aging are given.

Retarding deterioration of rubber. WM. S. CALCOTT and WM. A. DOUGLASS (to E. I. du Pont de Nemours & Co.). U. S. 1,789,696, Jan. 20. There is incorporated with the rubber a small proportion (suitably about 5%) of a reaction product of C_2H_2 with an amino compd. such as aniline, benzidine or *p*-aminophenol.

Working up scrap rubberized fabric. WARREN BROTHERS CO. Ger. 511,087, Jan. 21, 1926. Scrap rubberized fabric, e. g., automobile tires, is comminuted and then mixed at a raised temp. with mineral fillers and bituminous material. The compn. so obtained is suitable for road-making, roofing, etc. Details are given.

Hollow rubber articles. AYRTON SAUNDERS & CO., LTD., and F. TWELLS. Brit. 335,267, June 4, 1929. Articles formed of rubber over a foundation layer such as canvas are provided with a lining of different rubber compn. from the outer rubber facing and contg. about 5% carbon black so that it has a lower capacity for absorbing water.

Material for gas receptacles. A. GOLDBERG. Brit. 335,145, Feb. 5, 1929. A material suitable for making gas receptacles such as those used in respiration expts. comprises 2 rubber sheets with an intervening sheet of metal foil, either stuck or vulcanized together.

Artificial rubber. I. G. FARBENIND. A.-G. (Walter Bock and Eduard Tschunkur, inventors). Ger. 511,145, Jan. 15, 1927. See Brit. 283,840, (C. A. 22, 4274).

Coating compositions, etc., from synthetic rubber. I. G. FARBENIND. A.-G. Brit. 334,961, March 15, 1929. Polymerization products of diolefins produced as described in Brit. 333,872 (C. A. 25, 710) are hardened by any suitable method such as by the action of air or O in the presence of oxidation catalysts, treatment with $AlCl_3$ or action of S or S_2Cl_2 with or without vulcanization accelerators. The hardened material may be used for lacquer coatings, artificial threads, linoleum manuf., etc., with or without admixt. with other materials such as cellulose esters, natural or artificial resins, solvents, softening agents, waxes and drying oils. Numerous details and examples are given.

Polymerizing butadiene hydrocarbons. HANS LECHER and ALBERT KOCH (to I. G. Farbenind. A.-G.). U. S. 1,789,873, Jan. 20. An emulsion such as may be formed of isoprene and Na oleate soln. is homogenized before polymerization.

Rubber for dental purposes. CHRISTE JOANNIDES. Ger. 513,316, June 13, 1923. See Brit. 224,032 (C. A. 19, 1210).

Hollow articles of vulcanized rubber. I. G. FARBENIND. A.-G. (Wilfried Genth, inventor). Ger. 511,056, Mar. 22, 1928. See U. S. 1,765,666 (C. A. 24, 4186).

Vulcanizing rubber objects. ERNST WLCECK. Ger. 513,429, Jan. 16, 1927. Addn. to 452,466. According to Ger. 452,466, prepd. sheets or other rubber articles are vulcanized in the cold by alternate immersion in a 4-10% aq. SO_2 soln. and a satd. aq. soln. of H_2S . The treatment may be repeated as required. This method is now modi-

fied by adding to the rubber compn. a compd. which will liberate S when the article is immersed in a suitable bath. Thus, CaS and other sulfides may be added to the compn., and the article immersed in an aq. soln. of SO_2 .

Vulcanized products. JOSEPH C. PATRICK and NATHAN M. MNOOKIN. Fr. 692,235, Mar. 18, 1930. Rubber is mixed with a plastic material formed of a polysulfide and olefin (see Fr. 656,114, C. A. 23, 4030) and vulcanized by heat. The plastic material and free S are chosen so that the content of S in the product is at least 50%.

Vulcanizing core. DUNLOP RUBBER CO., LTD., and T. NORCROSS. Brit. 335,304, July 12, 1929.

Rubber vulcanization (air and steam supply and regulating system). MELVON A. MARQUETTE (to Fisk Rubber Co.). U. S. 1,790,011, Jan. 27. Various details of procedure are described.

Vulcanizing rubber. FREDERICK W. FARR. Fr. 692,172, Feb. 13, 1930. Rubber or like compns. are vulcanized in the cold by causing dild. S_2Cl_2 to pass through the whole thickness of the rubber, which is cut up into granules or little pieces to allow the penetration of the vulcanizing fluid, or fibrous material is agglomerated with the rubber to allow penetration of the fluid. Cf. C. A. 24, 3400.

Vulcanizing rubber. JOSEPH C. PATRICK. Fr. 691,743, Mar. 11, 1930. Rubber is vulcanized by heating it with a plastic compn. made by the reaction of an alkali polysulfide on a dihalogen olefin and contg. 75% or more of S. Compds. such as ZnO , $(\text{CH}_3)_3\text{N}_4$, Pb oleate and lampblack may also be added.

Vulcanizing rubber. I. G. FARBERIND. A.-G. Fr. 691,821, Mar. 12, 1930. The vulcanization of natural or artificial rubber is accelerated by adding to the mass to be vulcanized the products of the action of NH_3 on unsatd. aldehydes such as crotonic aldehyde, acrolein, methylpropylacrolein and ethylpropylacrolein.

Vulcanizing rubber, etc. SOCIETÀ ITALIANA PIRELLI. Fr. 691,456, Mar. 7, 1920. Rubber, ebonite, etc., are vulcanized by a preliminary heat treatment in molds and a subsequent complete vulcanization of the objects immersed in water in a suitable autoclave, carried to the vulcanization temp. and kept at a pressure greater than the characteristic pressure of satd. steam at that temp.

Rubber articles from latex. SOC. ITALIANA PIRELLI. Brit. 335,621, June 27, 1929. In a process generally similar to that described in Brit. 292,964 (C. A. 23, 1527), in which latex with a small proportion of certain added coagulants is subjected to local heating to produce coagulation, normal latex is heated to a moderate temp. (suitably 40–60°) and cooled prior to the introduction of the coagulants. Various details of procedure are given.

Rubber. I. G. FARBERIND. A.-G. (Curt Meisenburg, inventor). Ger. 511,540, Nov. 13, 1925. Liquid polymerized substances are removed from rubber-like condensation products (e. g., from butadiene) by treatment with powd. absorbents such as active C, active SiO_2 , etc.

Rubber, etc., dispersions. THE DUNLOP RUBBER CO., LTD., and THE ANODE RUBBER CO., LTD. Fr. 692,532, Mar. 21, 1930. In the manuf. of articles from org. dispersions of rubber, gutta-percha, balata or like vegetable resins, the surface of the molds or formers is covered with a film of dehydrating and coagulating liquid before immersion in the dispersions. Thus, the molds may be inserted in a concd. soln. of AcONH_4 , NaCl or NH_4Cl , to which an acid or a mixt. of acids may be added.

Rubber dispersions. NAUGATUCK CHEMICAL CO. Brit. 335,597, June 20, 1929. Rubber dispersions are prepd. as water-in-oil emulsions by emulsifying water in oil with suitable emulsifying agents and adding rubber before, after or during the emulsification, with subsequent mixing to effect dispersion. The products can be used in substantially the same manner as rubber-solvent doughs are used in making spread or coated fabrics. Numerous details and examples of procedure are given. Cf. C. A. 24, 751.

Preservation of rubber. WALDO L. SEMON (to The B. F. Goodrich Co.). Can. 308,541, Feb. 10, 1931. Rubber is preserved by treating with the resinous condensation product of $p\text{-C}_6\text{H}_4(\text{NHPh})_2$ with CH_2O . Cf. C. A. 24, 2329.

Rubber treatment to increase resistance to deterioration from age. WM. S. CALCOTT and WM. A. DOUGLASS (to E. I. du Pont de Nemours & Co.). U. S. 1,790,794, Feb. 3. Rubber compns. are treated, before vulcanization, with (as anti-aging addns.) 3-hydroxy-3-methoxybenzylamine (suitably 1–5%) or various other substances which may be obtained by the reaction of an aromatic primary amine with formaldehyde and a phenolic compd., as described in German patent 109,498. The resulting products are mixts. contg., in each instance as the major constituent, a hydroxybenzyl-aryl amine having the general formula $\text{R}-\text{NH}-\text{CH}_2-\text{R}'-\text{OH}$, in which R represents an aryl group which may or may not contain alkyl substituents and R' represents

an aryl group which may or may not contain alkyl and alkoxy substituents. Various examples and details of procedure are given.

Antioxidant for rubber. PAUL C. JONES (to The B. F. Goodrich Co.). Can. 308,542, Feb. 10, 1931. Rubber is preserved by incorporating with it tetraphenylhydrazine before vulcanization.

Rubber stock treatment. HENRY L. MORAN. U. S. 1,790,875, Feb. 3. Rubber stock is passed through a receptacle contg. water heated to about its b. p., to soften the rubber without cure or vulcanization. App. is described.

Apparatus for forming and calendering rubber or rubberized fabrics or strips. DUNLOP RUBBER CO., LTD., and H. WILLSHAW. Brit. 335,657, July 10, 1929. Mech. features and details of app. are described.

Sponge rubber. REGINALD J. NOAR. Ger. 515,340, May 26, 1928. See Brit. 284,938 (C. A. 22, 4877).

Ornamenting rubber articles. LIVERPOOL RUBBER CO., LTD., and G. THORNE. Brit. 335,612, June 28, 1929. Articles produced directly on a former from aq. dispersions of rubber, gutta-percha, balata or the like, are ornamented by dipping them while still on the former into water on the surface of which are floated streams of suitable colored solns. such as rubber solns. contg. pigments such as CdS or vermillion.

Regenerating rubber. LOUIS BEAUDOIN. Fr. 692,982, July 6, 1929. Waste rubber of all kinds is regenerated by heating it rapidly to 250-280° until the mass becomes bright; this change corresponds to the max. devulcanization which it is possible to obtain. An app. is described.

Substances resembling hard rubber. I. G. FARBERIND. A.-G. Fr. 692,606, Mar. 24, 1930. Substances resembling hard rubber are obtained by vulcanizing products obtained by the polymerization of erythrene. Examples are given.

Porous ebonite articles. MEYER WILDERMAN (to American Wilderman Porous Ebonite Co.). U. S. 1,791,437, Feb. 3. In forming porous articles such as diaphragms, the surface portions are formed of initially uncured ebonite occupying such volume that adjacent particles are in contact but are not compacted into a nonporous solid mass, the coatings of the particles being united by vulcanization between themselves and with the enclosed ebonite particles.

Synthetic rubber. I. G. FARBERIND. A.-G. Fr. 691,662, Mar. 10, 1930. A product resembling rubber is obtained by polymerizing 1,3-butadiene, a small quantity of water being added during the reaction. The water added may be in the form of water of crystn. in salts, e. g., $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ or $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$. Cf. C. A. 24, 6065.

Synthetic rubber. I. G. FARBERIND. A.-G. Brit. 335,616, June 29, 1929. Mixed rubber-like masses are produced by partially polymerizing a diolefin as described in Brit. 307,308 (C. A. 23, 5352), adding a different diolefin (such as 2,3-dimethylbutadiene if butadiene or isoprene is used as the initial material), and then further polymerizing. Various details and examples are given. Cf. C. A. 25, 1120.

Synthetic rubber compositions for tires. I. G. FARBERIND. A.-G. Brit. 334,958, June 15, 1929. Butadiene polymers used for tire manuf. as described in Brit. 299,037 (C. A. 23, 3376) are replaced by a mixt. of these polymers with a natural or artificial resin. Various details and examples are given.

Artificial rubber. I. G. FARBERIND. A.-G. (Helmuth Meis, Wilhelm Klein and Eduard Tschunker, inventors.) Ger. 515,143, July 21, 1927. Butadiene hydrocarbons, in aq. emulsion, are polymerized by addn. of a small quantity of a finely divided or colloidal heavy metal oxide which does not yield H_2O_2 when treated with acids. MnO_2 and PbO_2 are suitable oxides. Protective colloids may be included in the emulsions, and the oxide may be formed *in situ*. Examples are given.

Vulcanizing rubber. IMPERIAL CHEMICAL INDUSTRIES, LTD. Fr. 693,178, April 2, 1930. Rubber and like substances and vulcanizable oils are vulcanized in the presence of an *N,N*-dithio deriv. of a secondary amine such as *N,N*-dithiopiperidine.

Rubber. IMPERIAL CHEMICAL INDUSTRIES, LTD. Fr. 693,975, April 7, 1930. The deterioration of rubber and like compds. is retarded by mixing with the unvulcanized rubber an org. N. compd. capable of sepg. into free radicals contg. bivalent N such as tetraphenylhydrazine or *N*-triphenylmethylidiphenylamine and afterward vulcanizing.

Creaming rubber latex. K. D. P., LTD. Brit. 337,269, Jan. 24, 1929. Concn. of latex is effected by adding to it materials such as mucilages of Carrageen moss, Iceland moss or diatom adapted to combine with water without previous hydrolysis and heating to above 60° to cause creaming.

Electrodeposition of rubber. DUNLOP RUBBER CO., LTD., D. F. TWISS, A. A. ROUND and E. W. MADGE. Brit. 336,659, July 18, 1929. Rubber or other org. material is deposited from an aq. dispersion by use of a c. connected to rectifying elec-

trodes, one of which is preferably Al or Ta while the other may be of Zn or C. The liquid in contact with the rectifying electrode preferably contains an electrolyte such as an alkali metal phosphate or borate which may be held in a gypsum or unglazed earthenware vessel surrounding the electrode.

Rubber compositions. I. G. FARBERIND. A.-G. Brit. 337,095, Aug. 12, 1929. A rubber compn. of good mech. strength is obtained by compounding with polymerization products such as those of butadiene or isoprene the solid substance obtained by removing the low b. p. constituents from the product of the careful low-temp. carbonization of bituminous material such as brown coal. The low b. p. constituents may be removed from the added material by distn. under reduced pressure or by extn. with acetone and the resulting material may be treated with vapors contg. O or S compds. or with S, phthalic anhydride, ZnO or other substances having a condensing action. Cf. C. A. 24, 4186, 5535.

Purifying gutta percha and like materials. W. S. SMITH, H. J. GARNETT and J. N. DEAN. Brit. 335,966, June 6, 1929. Crude gutta percha, balata or the like is subjected to selective extn. with a solvent acting selectively on the resins at a suitable temp. to remove the fluavil and like resins and leave behind resins of the Albane type. Gutta percha may be treated with EtOH at 21° or with acetone at 3° in prep. an elec. insulating product.

Rubber mixtures. RUDOLF DITMAR. Austrian 120,423, July 15, 1930. Esters of adipic acid and its derivs. are used as plasticizers for rubber. Cyclohexyl and methylcyclohexyl adipates and methylcyclohexyl methyladipate are specified.

Method of determining the plasticity and adhesion of rubber, etc., by extrusion under heat and pressure. HYDRAULIK G. M. B. H. and FRIEDRICH W. KOERVER. Ger. 516,203, Dec. 9, 1928.

Coloring rubber. I. G. FARBERIND. A.-G. and J. Y. JOHNSON. Brit. 336,446, Oct. 29, 1929. There is rolled into solid rubber such as crepe rubber one of the water-sol. components of a practically water-insol. dye, *e. g.*, 2,3-hydroxynaphthoic acid *o*-anisidide, and the dye is then pptd. within the material, *e. g.*, by use of the diazo compd. of 5-nitro-2-toluidine. Various details of procedure are described.

Coloring rubber and rubber substitutes. I. G. FARBERIND. A.-G. Brit. 335,912, May 29, 1929. Rubber substitutes made from fatty oils such as vulcanized rape-seed oil or mixed factice and linseed oil are mixed, in the form of an emulsion or suspension, with aq. pastes of org. or inorg. water-insol. coloring materials, or with dry pigments, lakes, water-insol. metal salts of org. dyes or their mixts., or with leuco compds. of vat dyes, or with reagents forming a color lake or the like *in situ* and the colored material is simultaneously or subsequently coagulated, and may be further used for coloring rubber or other plastic materials. Wetting agents such as alkyl-naphthalene-sulfonic acids or their salts may be used to facilitate the process. Cf. C. A. 24, 4185, 6064.

Colored rubberized fabrics. JAMES J. CLIFFORD (to Steadfast Rubber Co.). U. S. 1,792,277, Feb. 10. For durably uniting coloring pigment to a rubber-compd.-coated fibrous fabric there is applied a non-oleaginous pigment mixt. such as Au, Ag or bronze powder together with nitrocellulose and a solvent including AmOAc and a blending ingredient such as benzene or high-test naphtha.

Coating metals or other materials with rubber. H. BECKMANN. Brit. 337,222, Nov. 14, 1929. Materials such as metals, stone, wood or cement are provided with a thin layer of rubber having exceedingly fine pores, several alternative processes for producing which are described.

Rubber product resistant to aging. WINFIELD SCOTT (to Rubber Service Laboratories Co.). U. S. 1,792,042, Feb. 10. Prior to vulcanization, there is incorporated with the rubber compn. a S deriv. of a reaction product of a ketone and a naphthylamine such as that of acetone and α -naphthylamine.

Rubber articles. DUNLOP RUBBER CO., LTD., and THE ANODE RUBBER CO., LTD. Fr. 694,676, Apr. 29, 1930. Articles are made of rubber or like material having a spongy or cellular structure, by starting with aq. emulsions or dispersions, particularly those which may be converted to a gel by heating or those to which substances have been added which will form a gel after a definite time in the cold, and transforming them into a froth or foam by a gas or by energetic stirring.

Rubber articles. DUNLOP RUBBER CO., LTD., and THE ANODE RUBBER CO., LTD. Fr. 694,768, April 30, 1930. Articles are made of rubber or the like of a spongy or cellular texture from aq. emulsions or dispersions in the state of foam contg. a gas (the emulsions or dispersions being still in the reversible state) and solidifying the foam to form a permanent mass of solid and stable material.

Hollow rubber articles. SOCIETÀ ITALIANA PIRELLI. Fr. 694,993, May 5, 1930.

A core for hollow rubber articles is made of colloidal materials such as foundry earths, chalks, clay and kaolins, molded with the amt. of water strictly necessary and baked.

Inflated rubber articles such as balls. MURRELL J. DE FRANCE (to Pennsylvania Rubber Co.). U. S. 1,792,362, Feb. 10. A hollow blank is formed of incompletely vulcanized rubber, coated interiorly with successive layers of gelatin and of rubber, water and reactive gas-generating substances such as NaNO_2 and NH_4Cl are inclosed within the blank and the latter is subjected to a vulcanizing temp. in a mold.

Rubber rollers. R. WHEATLEY and VICTORIA RUBBER CO., LTD. Brit. 337,250, May 30, 1930. The under layers of rubber-covered rollers are formed of sponge rubber of the isolated gas-filled pore kind.

Rubber footwear. CHARLES M. RICHARDSON and ARTHUR J. HOWE (to B. F. Goodrich Co.). U. S. 1,792,322, Feb. 10. Mech. features and an arrangement of app. are described.

Rubber boot manufacture. HOOD RUBBER CO. Brit. 336,226, July 8, 1929. A layer of relatively non-flowing material such as a mixt. of rubber with fibrous material is placed next to the lining to prevent the rubber or the like of the boot leg from filling the spaces between the threads of the lining, to reduce the stiffness of the boot and to prevent adhesion to the last. Various details of manuf. are described.

Use of forms in making balloons, gloves, coats or other dipped rubber goods from aqueous dispersions of rubber. ISAAC W. ROBERTSON (to Thermo Process Co.). U. S. 1,792,187, Feb. 10. Various details of procedure are described.

Puncture-sealing mixture for tires. P. G. MASTERS. Brit. 335,980, July 5, 1929. A mixt. for placement in inner tire tubes is formed of castor oil 0.5 pint, talc 1.5 oz., cellulose 1.5 oz., such as wood dust, water 0.5 pint, gum acacia 1 oz. or less, with or without a small addn. of benzene, "petrol" or rubber soln.

Rubber insulating material. WM. BRYAN WIEGAND. Fr. 694,333, April 23, 1930. Insulating materials contg. rubber have added thereto C black retaining its adsorbent power in amt. up to 10% of the wt. of rubber or 3% of the total mass. An example of such a material contains rubber 984.6, ZnO 30, C black 29, monosulfide of tetramethylthiouran 3.5 and S 40 parts. Other examples are given.

Mercaptothiazole derivatives. WM. P. TER HORST (to Rubber Service Laboratories Co.). U. S. 1,792,096, Feb. 10. In producing products such as various rubber vulcanization accelerators, reaction is effected between an amine such as piperidine or diphenylguanidine and the product obtained by the reaction a salt of mercaptobenzo-thiazole with a Cl deriv. of CS_2 . Cf. C. A. 24, 2470.

Elastic material. OCTAVE PIRARD. Fr. 694,998, Aug. 2, 1929. A light elastic material is made, e. g., of wood charcoal 35, bark fiber 10 and pure rubber 55%.

Transparent sheets comprising synthetic rubber. I. G. FARBENIND. A.-G. Brit. 336,075, Sept. 20, 1929. Reinforced sheets are made by applying a soft coating of a polymerization product of butadiene or its homologs to an open-meshed fabric (such as tinned iron wire mesh or a vegetable fiber material) and hardening the coating (as by the action of O or by heating). Condensation products such as those derived from oxylene or other aromatic hydrocarbons with butadiene in the presence of a condensing agent such as AlCl_3 also may be used.

Synthetic rubber. I. G. FARBENIND. A.-G. Brit. 336,339, Aug. 2, 1929. Removal of polymerization products of diolefins from the reaction vessel is facilitated by lining the vessel with readily removable materials such as paper, cardboard, textile fabrics, leather, or films of sheet metal or cellulose derivs. or polymers of diolefins or of rubber (which latter may be vulcanized or otherwise suitably treated), or waxes, readily fusible alloys or bitumen. Various examples and details of app. and procedure are given.

Synthetic rubber. I. G. FARBENIND. A.-G. Brit. 337,019, May 25, 1929. In polymerizing diolefins such as butadiene by the action of alkali or alk. earth metals or their mixts. or alloys, in the presence of org. solvents such as ether, the solns. of the polymerization products are continuously removed from the catalyst as soon as the polymerization is effected, as by a flowing stream of solvent or soln. The products may be unsuitable for the production of soft rubber, but are suitable for the manuf. of various hard materials.

Vulcanizing synthetic rubber. I. G. FARBENIND. A.-G. Brit. 335,970, July 2, 1929. Polymerization products such as those of butadiene or its homologs or analogs are vulcanized in the presence of an accelerator previously dissolved in a solvent or admixed with a liquefying agent, which gives a product of improved stretch and breaking strength. Solvents of various kinds may be used such as water, alc., hydrocarbons, chlorinated hydrocarbons, ethers, weak acids and liquid bases. Stearic acid may be used as a softening agent. Cf. C. A. 24, 3400.

Rubber vulcanization accelerator. WINFIELD SCOTT (to Rubber Service Labora-

tories Co.). U. S. 1,792,041, Feb. 10. The reaction product of formaldehyde with crotonaldehyde dianilide is used as an accelerator. Cf. C. A. 25, 618.

Rubber vulcanization. ALBERT A. SOMERVILLE (to R. T. Vanderbilt Co.). U. S. 1,791,876, Feb. 10. In effecting vulcanization with the aid of an active accelerator such as mercaptobenzothiazole a small quantity of a peroxide such as BaO_2 , PbO_2 , CaO_2 or SrO_2 is added to inhibit or prevent scorching or prevulcanization. Various examples are given.

Apparatus for vulcanizing rubber coatings on hollow metal articles such as press-rollers of paper-making apparatus. CHRISTIAN H. GRAY. U. S. 1,792,298, Feb. 10. Structural features.

Forming vulcanized joints in rubber articles such as air-tubes, rubber balls or other hollow products. DUNLOP RUBBER CO., LTD., and G. R. MEAD. Brit. 336,076, Sept. 21, 1929. Mech. features.

Rubber. I. G. FARBERIND. A.-G. (Julius Eisele and Johannes Stöhrle, inventors). Ger. 517,490, Sept. 13, 1927. Rubber latex is rapidly mixed with sufficient acid to establish a hydron concn. greater than p_H 2, preferably greater than p_H 1, and a compd. reducing the surface tensions is then added, e. g., Na β -naphthalenesulfonate or Turkey-red oil. The mixt. sets to an irreversible gel with sepn. of a small quantity of clear serum. Vulcanizing agents, accelerators or fillers may be added before or after the formation of the gel. Examples are given. Cf. C. A. 25, 1706.

Rubber. SOCIETÀ ITALIANA PIRELLI. Ger. 517,208, Oct. 12, 1926. The aging properties of rubber are improved by addn. of about 5% of the evapn. residue of latex serum from which quebrachitol has been removed, e. g., by crystn. Albumins may also be removed from the serum to be evapd., e. g., by pptn. with tannic acid.

Rubber deposition. IMPERIAL CHEMICAL INDUSTRIES, LTD., and R. B. F. F. CLARKE. Brit. 337,946, Oct. 21, 1929. A hollow gas-permeable vessel, filled with CO_2 under pressure, is immersed in latex, and rubber is deposited on it as the CO_2 diffuses through the walls of the vessel and effects coagulation of the rubber deposit. Material to be impregnated may be wrapped around the vessel, and the vessel may be shaped to produce sheets or articles of other desired form.

Rubber composition. ELLWOOD B. SPEAR and ROBERT L. MOORE (to Thermo-tomic Carbon Co.). U. S. 1,794,558, March 3. A C black of the kind designated as "P-33" is used in making a rubber compn. having an ultimate tensile strength approx. the same as a similar rubber compn. contg. an equal wt. of "common com. C black" but having a stiffness materially less than such a rubber compn. An app. is described suitable for making the C from hydrocarbon gas. Cf. C. A. 24, 212.

Rubber compositions. E. O. COWPER. Brit. 338,247, June 5, 1929. Compns. suitable for covering athletic grounds, for use as *expansion joints, wall and roof coverings, machinery beds, etc.*, are formed of latex from which the serum constituents have not been removed, mixed with waste rubber, rubber scrap, old tire stock or the like and with breeze, ashes, clinker, brick dust, baked clay, slate dust or the like; vulcanizing materials, pigments and bituminous or portland cement, etc., may also be added, as may also fibrous fillers. The material may be placed on a backing such as cloth or paper coated with bituminous material. Various details and examples are given.

Rubber composition suitable for tire treads, shoe soles, etc. ARTHUR B. COWDERY and THEODORE A. BULIFANT (to Barrett Co.). U. S. 1,793,161, Feb. 17. There is incorporated in a rubber mixt. a coal tar substantially free from cryst. material at 25° having a sp. gr. above 1.06 at 38° and b. above 200°. Cf. C. A. 24, 1545.

Coloring rubber. I. G. FARBERIND. A.-G. (Rudolf Krech, inventor). Ger. 517,450, Sept. 5, 1926. Rubber is mixed with an insol. metal salt of Patent Blue A, which may be deposited on a substrate. The colors obtained are fast to vulcanization. Examples are given.

Coloring rubber. DUNLOP RUBBER CO., LTD., D. F. TWISS, E. A. MURPHY and R. G. JAMES. Brit. 338,303, Oct. 11, 1929. Rubber articles obtained from aq. dispersions by dipping, spreading, painting, extruding, spraying, electrophoresis impregnating or molding are colored, locally or generally, after formation, by reaction between successively added substances which together form a desired coloring substance and one of which if desired may be added to the initial dispersion, e. g., β -naphthol may be initially added and subsequently combined with a diazo soln., or the formed article may be dipped in indigo white soln. and subsequently oxidized, or an article formed by use of acid may be dipped in an alk. sulfide soln. of a S dye.

Preserving rubber. MARION C. REED (to B. F. Goodrich Co.). U. S. 1,793,635, Feb. 24. *Asym*-diphenyl- or other diaryl-hydrazine (suitably in the proportion of about 0.1-5.0%) is added to rubber compns. as a preservative.

Rubber dispersions, etc. DOUGLAS F. TWISS and EDWARD A. MURPHY (to Dunlop Rubber Co., Ltd.). U. S. 1,793,265, Feb. 17. For the production of substantially reversible compns. of pasty consistency from aq. dispersions contg. rubber or similar materials and a protective colloid, the dispersions are evapd. in the presence of one or more substances such as glycerol, glycol or a glycol alkyl ether, having as their principal function to serve in place of water as a medium in which the protective colloids, both naturally occurring and artificially incorporated, will continue to function when the water in the dispersions is substantially removed.

Making thin rubber bathing caps. MELVIN S. LOWER (to Sun Rubber Co.). U. S. 1,794,192, Feb. 24. App. and various details (mainly of mech. character) are described.

Rubber footwear. JAMES B. CROCKETT (to Cambridge Rubber Co.). U. S. 1,795,075, March 3. A last is dipped into an aq. rubber-contg. material contg. a coloring agent to form a deposited coating on the last, and the coated last is then dipped in an aq. rubber compn. of different coloring and the sole portion of the article is selectively dipped in an aq. rubber compn. contg. fillers for increasing the resistance of the sole to wear.

Molded rubber footwear. H. C. L. DUNKER. Brit. 337,831, Aug. 9, 1929. Articles such as galoshes or "seaside shoes" are formed by molding over a prevulcanized lining drawn onto the last and there covered with unvulcanized rubber to be molded.

Rubber battery boxes, etc. J. FERGUSON & SONS, LTD., and J. E. FERGUSON. Brit. 338,114, July 10, 1929. Boxes are formed in such a way that the sides are harder than the base (as by subjecting the sides to a higher heat than the base in the vulcanization); they may be made of raw rubber or of waste rubber from old tires, mixed with S, ZnO, an accelerator such as diphenylguanidine and a lubricant such as paraffin. Various details of manuf. are given.

Rubber cement. THEODORE WHITTLESLEY. U. S. 1,793,983, Feb. 24. Rubber latex is used with a solvent such as C_6H_6 and a small quantity of an emulsifying agent such as Na oleate, which facilitates diln. of the cement with water.

Synthetic rubber. I. G. FARBERIND. A.-G. Brit. 337,460, Aug. 2, 1929. Alkali metal such as Na used in effecting polymerization of diolefins is enclosed in a small perforated container (which may be formed of glass or metal) placed within the reaction vessel. When the small perforated container becomes filled with polymerizate the latter with some assocd. alkali metal is forced out into the main reaction vessel to promote further polymerization of its contents. The process may be carried out in 2 stages and a diluent such as diethylene dioxide may be used.

Synthetic rubber. I. G. FARBERIND. A.-G. Brit. 338,152, May 14, 1929. Polymerization of diolefins such as butadiene is effected with at least 30% of an inorg. O-contg. acid or an org. deriv. of such an acid (without addn. of any other substance influencing the reaction). Among the substances which may be used are: H_2SO_4 , H_3PO_4 , benzenesulfonic acid, toluenesulfonic acid, *p*-toluene sulfonylchloride and benzene sulfonylchloride. Products of varying character are obtained by varying the conditions of the reaction, and they may be suitable for adhesives, as *addns. to paints or lacquers*, *manuf. of threads, films*, molded articles, etc. Several examples with details of procedure are given.

Rubber-like product. JEAN BAER. Swiss 142,456, Jan. 8, 1929. A rubber-like mass is obtained by treating an isoprene halide with alkali or alk. earth polysulfides. In the example, isoprene dibromide is treated with K_2S_8 . Cf. C. A. 24, 1545.

Factice. JEAN BAER. Swiss 142,354 to 142,357, June 19, 1928. Addns. to 137,477 (C. A. 24, 4426). Factice sol. in hydrocarbons is prep'd. by heating the rubber-like mass from CH_2Cl_2 and a polysulfide soln. with an oil such as rapeseed oil. The CH_2Cl_2 may be replaced by $C_6H_4Br_2$, CH_2Br_2 or CH_2O .

Rubber vulcanization accelerators. ALBERT M. CLIFFORD (to Goodyear Tire & Rubber Co.). U. S. 1,792,819, Feb. 17. As an accelerator, there is used the reaction product of cyclohexylamine and an aldehyde such as aldol, butyraldehyde, crotonaldehyde, heptaldehyde or formaldehyde.

Rubber vulcanization accelerators. LORIN B. SEBRELL and DEXTER N. SHAW (to Goodyear Tire & Rubber Co.). U. S. 1,792,770, Feb. 17. *o*-Tolylamidoxime or other compds. of the general formula $RC(:NOH)NH_2$, in which R represents a benzene group, are used as accelerators.

Rubber vulcanization accelerators. JAN TEPPEMA (to Goodyear Tire & Rubber Co.). U. S. 1,792,780, Feb. 17. Vulcanization with S is effected in the presence of the reaction product of mercaptobenzoxazole and a basic amine such as diphenylguanidine. Cf. C. A. 24, 3135.

Apparatus for vulcanizing lengths or sheets of rubber or rubberized material.

HARRY WILLSHAW and WALTER G. GORHAM (to Dunlop Rubber Co., Ltd.). U. S. 1,793,269, Feb. 17. Structural features.

Purifying latex. K. D. P., LTD. Brit. 338,766, Dec. 20, 1928. Latex is subjected to heat treatment with simultaneous evapn. and then subjected to a usual purifying treatment, as by centrifuging to sep. serum, which is facilitated by the pretreatment.

Device for spraying rubber latex by an air jet. CHARLES E. MAYNARD (to Fisk Rubber Co.). U. S. 1,795,875, March 10. Structural features.

Rubber. K. D. P., LTD. (Rudolf Pummerer and Hans Kroepelin, inventors). Ger. 515,603, May 26, 1926. Addn. to 460,950. Pure rubber hydrocarbons are prepd. from rubber latex by treating with alkali in an electrodialyzer.

Rubber compositions. DUNLOP RUBBER CO., LTD., E. A. MURPHY, A. NIVEN and D. F. TWISS. Brit. 338,975, Aug. 30, 1929. Crumb-like rubber compns. are prepd. by coagulating an aq. dispersion of rubber or the like, by pptn. *in situ* (in relatively large amounts on the dry rubber content) of compounding ingredients formed by the interaction of one or more water-sol. reagents normally having no coagulating effect, with other added water-sol. reagents, such as reagents which together form products such as $MgCO_3$, $CaCO_3$, $ZnCO_3$, Ca, Ba or Zn silicates, silicic acid or Zn, Cd or Pb sulfides. Soap, glue, gum acacia, etc., may be added to modify the properties of the product.

Use of amines as rubber coagulants. ALBERT J. GRACIA (to Goodyear Tire & Rubber Co.). U. S. 1,797,192, March 17. Latex is coagulated by use of amines such as ethylamine, diethylamine, propylamine, dipropylamine, tripropylamine, butylamine, amylamine, iso-amylamine, di-isoamylamine or allyl amine.

Preserving rubber. LORIN B. SEBRELL (to Goodyear Tire & Rubber Co.). U. S. 1,797,179, March 17. Anilinoxylylideneaniline (suitably in the proportion of about 0.5%) is added to rubber compns. before vulcanization.

Rubber "antioxidant." WM. S. CALCOTT and WM. A. DOUGLASS (to E. I. du Pont de Nemours & Co.). U. S. 1,796,980, March 17. Deterioration of rubber is retarded by the addn. of a small proportion (suitably about 0.5-2.5%) of a transparent brittle solid obtained by the reaction of glucose on *m*-tolylenediamine.

Trinaphthylamine. ALBERT M. CLIFFORD (to Goodyear Tire & Rubber Co.). U. S. 1,797,196, March 17. This compd. is obtained by extrn. with C_6H_6 from crude dinaphthylamines and is an antioxidant for rubber.

"Micro-porous" rubber. H. BECKMANN. Brit. 338,698, Oct. 26, 1928. The process described in Brit. 240,430 (C. A. 20, 2262) is modified by adding to the latex a substance capable of being coagulated to form a hydrophilic gel, such as 2% of blood albumin, and then adding a coagulating agent, such as HOAc, which will cause coagulation of both the latex and the added substance. Among the substances which may be added are: silicic acid, stannic acid, $Al(OH)_3$, colloidal Fe_2O_3 , colloidal chromic oxide, colloidal tungstic and molybdic acids, manganic hydroxide, V pentoxide, albuminoids, polypeptides and hemoglobin, and substances such as silicic acid may be formed in the latex by reaction. Cf. C. A. 24, 752.

Apparatus for molding rubber articles such as tennis balls. HARRY WILLSHAW and SYDNEY N. GOODHALL (to Dunlop Tire & Rubber Corp.). U. S. 1,795,917, March 10. Various structural features are described.

Uniting rubber and leather. K. EHMKE. Brit. 338,789, Jan. 8, 1930. Materials such as shoe parts of rubber are roughened on a grinding wheel, coated with rubber soln., sprayed with particles of crepe rubber and further coated with rubber soln. and then united by hammering with leather coated with rubber soln.

Attaching rubber to metals. C. M. CARSON (to Goodyear Tire & Rubber Co.). Brit. 339,421, Feb. 23, 1929. A cement is used consisting of latex, hemoglobin, a tanning agent such as formaldehyde, $K_2Cr_2O_7$, $K_4FeC_6N_6$ or $Al_2(SO_4)_3$, and vulcanizing ingredients and this cement is vulcanized after application.

Compositions containing rubber and cement. N. SWINDIN and NORDAC, LTD. Brit. 339,002, Sept. 5, 1929. In making a material suitable for floors, road surfaces or acid-resisting coating, raw rubber (heated or swelled with a solvent) is dispersed with water (preferably in the presence of a hard porous inert powder such as fine coke dust which acts as a tritulating agent), suitably with addn. of emulsifying agents such as soap, saponin, borax, NH_3 and soda, and the material is then mixed with a cement (such as portland or oxychloride cement materials) which reacts with the water and causes setting of the mass. Various details and use of different fillers, etc., are described.

Films, threads, disks, etc. I. G. FARBENIND. A.-G. Fr. 37,485, Oct. 3, 1929. Addn. to 676,658 (C. A. 24, 3135). Mixts. of natural rubber with the polymerization products of butadiene hydrocarbons are treated with sulfurizing agents until the high elasticity characteristic of rubber disappears.

Isomerizing rubber. IMPERIAL CHEMICAL INDUSTRIES, LTD., and E. B. ROBINSON. Brit. 339,398, Sept. 30, 1929. Rubber is liquefied by heat and then treated with isomerizing substances such as H_2SO_4 , sulfonic acids, sulfonyl chlorides, sulfuric esters or metallic halides, with or without phenolic compds., to produce a thermoplastic product. Various details of procedure are given.

Apparatus for curing tire flaps. ROBERT W. SNYDER (to Goodyear Tire & Rubber Co.). U. S. 1,797,180, March 17. Structural features.

Rubber conversion product. HERMAN A. BRUSON (to Goodyear Tire & Rubber Co.). U. S. 1,797,188, March 17. See Can. 299,963 (C. A. 24, 3135).

Synthetic rubber. I. G. FARBERIND. A.-G. Brit. 338,534, Aug. 17, 1929. Polymerization of diolefins such as butadiene is effected in the presence of alkali or alk. earth metals or their alloys in particles of uniform size, such as with Na balls of 1.1 mm. diam. in a rotating Fe autoclave at 40°.

Synthetic rubber. I. G. FARBERIND. A.-G. Brit. 339,135, Dec. 20, 1929. Polymerization of diolefins such as butadiene with an alkali metal such as Na is effected in the presence of at least 25% of a low b.-p. aliphatic ether such as dimethyl, diethyl or methylethyl ether (these ethers serving both as diluents and as catalysts). Various details and examples are given.

Synthetic rubber. I. G. FARBERIND. A.-G. Brit. 339,243, Aug. 30, 1929. Polymerization of diolefins such as butadiene is effected in the presence of alkali or alk. earth metals or their alloys such as Na amalgam or of alkali or alk. earth metal compds. with org. radicals which are not capable of ionization (such as Na ethyl, K ethyl, K diphenylmethylmethane, Na triphenyl methane and Li alkyls) and the polymerization agent is added gradually or in at least 3 successive portions during the polymerization. The polymerizing agent may be mixed with other substances such as polymers of diolefins, rubber, paraffin, salt or waxes. Several examples are given.

Synthetic rubber. I. G. FARBERIND. A.-G. Brit. 339,255, Aug. 30, 1929. Rubber-like products suitable for various purposes similar to those for which rubber is usually employed are obtained by polymerizing a mixt. of a diolefin such as erythrene, isoprene, butadiene, methyl- or dimethyl-butadiene, with styrene (suitably after emulsification of the initial materials together with Na stearate or other suitable emulsifying agent). The polymerization may be carried out at 40-60° for several days, and products of different properties may be produced by varying the proportions of the starting materials.

Synthetic rubber. I. G. FARBERIND. A.-G. Fr. 37,374, Aug. 29, 1929. Addn. to 655,217 (C. A. 23, 4103). Synthetic rubber, etc., is intimately mixed with finely divided soot such as lampblack or C black before vulcanization.

Thiuram disulfides. GEORGE C. BAILEY (to Roessler & Hasslacher Chemical Co.). U. S. 1,796,977, March 17. Compds. suitable for use as rubber vulcanization accelerators and having the general formula $R_1-CS-S-CS-R_1$ are made by treating a compd. of the type $R_1-CS-S-M$ with NaOCl, R_1 comprising an org. radical and M a metal radical. Tetramethylthiuram disulfide is made by treating Na dimethyldithiocarbamate with NaOCl in aq. soln.

Rubber vulcanization accelerators. RUBBER SERVICE LABORATORIES, INC. Brit. 339,352, Sept. 7, 1929. Accelerators are prepd. by reaction of an aldehyde amine such as butylidene isoamylamine with a substituted unsatd. aldehyde such as α -ethyl- β -propylacrolein. Various details of procedure for manuf. and use of the accelerator are described. Cf. C. A. 24, 266,752.

Apparatus for vulcanizing automobile tires. MATTHEW REID. U. S. 1,795,680, March 10. Structural features.

Vulcanizing rubber. INDUSTRIAL PROCESS CORP. Brit. 339,303, Nov. 26, 1928. See Fr. 681,061 (C. A. 24, 4426).

Vulcanizing rubber. HAROLD GRAY (to B. F. Goodrich Co.). U. S. 1,796,018, March 10. A product formed by reaction of an org. amine such as aniline or NH_3 , 1, and an aliphatic aldehyde such as butyric aldehyde 3 or more mol. proportions is used as an accelerator.

Rubber vulcanization. ADRIEN CAMBRON (to Roessler & Hasslacher Chemical Co.). U. S. 1,796,240, March 10. An accelerator is used comprising the product obtained by causing aniline and acetaldehyde, under essentially anhyd. conditions, to react in the presence of a small quantity of $ZnCl_2$. Cf. C. A. 24, 2640.

Vulcanized colored rubber. RUDOLPH KEECH (to I. G. Farbenind. A.-G.). U. S. 1,796,656, March 17. Before vulcanization, there is incorporated with rubber an insol. metal salt such as the Ba salt of an acid anthraquinone dye contg. at least one amino group, such as 1-amino-4-phenylaminoanthraquinone-2-sulfonic acid, and the material is then vulcanized.

Rubber. ALBERT C. BURRAGE, JR. Fr. 697,090, June 4, 1930. Oxidation or aging of vulcanized rubber is prevented or reduced by substituted nitrosoamines such as diphenylnitrosoamine, phenyltolyl nitrosoamine, di- α -naphthyl nitrosoamine, etc.

Porous rubber. K. D. P., LTD. Ger. 521,307, Mar. 31, 1928. Latex is converted by mech. means into foam, if desired with the aid of a foaming agent, and the foam is vulcanized. Thus, a mixt. of latex, S, ZnO and an accelerator may be agglomerated with $(\text{HCOO})_2\text{Ca}$ soln. and the mass beaten to a stable foam after addn. of saponin. The foam is charged into molds and vulcanized.

Rubber latex. I. G. FARBENIND. A.-G. Ger. 519,483, Nov. 12, 1926. Salts of true sulfonic acids having good wetting properties are used as preservatives for rubber latex, alone or with other preservatives. The salts may be used also as assistants in the *impregnation of fabrics, cork, paper*, etc., with latex. Examples are given.

Coagulating latex. METALLGES. A.-G. Fr. 695,786, May 17, 1930. Latex is coagulated by adding substances which do not on addn., have a thickening or coagulating action, but which on a change of phys. conditions such as change of temp. introduce substances which have a coagulating action in an amt. sufficient for the coagulation of the latex. A complex salt which gives a coagulating ion on dissocn. by heat, a salt which dissoc. on heating to give an acid, or a coagulant protected by a layer of inert adsorption substance which is removed by heat may be used.

Rubber inner tubes from latex. EDWIN B. NEWTON (to American Anode, Inc.). U. S. 1,797,240, March 24. Various details are described of uniting valve pads of masticated rubber to wet coagulated tubes, pressing, drying and vulcanizing.

Electrodeposition of rubber, etc. THE ANODE RUBBER CO. Ger. 520,323, April 30, 1926. See Brit. 253,085 (C. A. 21, 2438).

Preserving rubber. MARION C. REED (to B. F. Goodrich Co.). U. S. 1,797,241, March 24. An addn. product of an aromatic nitro compd. such as dinitrochlorobenzene with a secondary aromatic amine such as phenyl- β -naphthylamine is added to rubber compns. as a preservative (suitably in the proportion of about 0.5%). Various other examples are given also. Cf. C. A. 25, 2331.

Rubber preservation against aging. P. C. JONES (to B. F. Goodrich Co.). Brit. 339,834, Jan. 21, 1929. Aging is retarded by adding tetrasubstituted hydrazines (several of which are mentioned as suitable) to latex, to rubber before vulcanization or to the surface of rubber after vulcanization. Some description of the manuf. of these preservative substances also is given. Cf. C. A. 25, 617.

Rubber dispersion. WALDO L. SEMON and RICHARD A. CRAWFORD (to B. F. Goodrich Co.). U. S. 1,797,243, March 24. A mixt. of rubber 100, benzene 10-100, glue 1 and casein 1 part is masticated while slowly adding an aq. soln. of K oleate until the rubber constitutes the dispersed phase of the batch. The product is suitable for use as a cementing medium. Cf. C. A. 24, 2918.

Filtering apparatus suitable for filtering rubber dispersions. ANDREW SZEGVARI and CHARLES M. SPENCER (to American Anode Inc.). U. S. 1,797,248, March 24. Structural features of an app. having a filtering material such as a textile fabric strip.

Apparatus for making spongy articles from organic dispersions. THE DUNLOP RUBBER CO., LTD., and THE ANODE RUBBER CO., LTD. Fr. 696,176, May 27, 1930.

Coloring rubber, etc. I. G. FARBENIND. A.-G. (Arwin Ranft, inventor). Ger. 506,207, Nov. 14, 1924. Addn. to 462,221. Natural or synthetic rubber, gutta-percha or balata is colored with water-insol. vat, sulfur or azo dyes or lakes by incorporating in the rubber, etc., an aq. soln. of the leuco compd. or other sol. modification of the dye, or an aq. soln. of the dye or lake components, and then converting the leuco compd., etc., into the insol. dye or lake in known manner. Examples are given. Cf. C. A. 25, 2021, 2331.

Light rubber board. DUNLOP RUBBER CO., LTD., and E. W. MADGE. Brit. 340,024, Sept. 19, 1929. Light rubber board suitable for use in airplane and speedboat construction comprises one or more porous layers of hard rubber (obtained from aq. dispersions) sepg. 2 or more layers of metal, ebonite, ebonite-coated metal, fabric-reinforced ebonite or ebonite-impregnated fabric or "doped fabric" or plywood. The aq. dispersions used may contain rubber, gutta-percha, balata and similar vegetable resins, natural or artificial, vulcanized or unvulcanized, etc. Various details of manuf. are described.

Forming rubber tubes suitable for use as tire inner tubes. ERNEST HOPKINSON and WILLIS A. GIBBONS (to Morgan & Wright). U. S. 1,797,580, March 24. An aq. dispersion of rubber is placed in contact with a surface of a tubular form of fibrous material such as woven fabric and fluid from the dispersion is withdrawn through the form to deposit solids from the dispersion in tubular shape on the form; the thickness of the deposit adjacent to its ends is gradually reduced to form skived ends, the deposit

is dried and removed, and its skived ends are united. App. is described, as are also various compns. used.

Rubber threads. DUNLOP RUBBER CO., LTD., W. G. GORHAM and E. A. MURPHY. Brit. 339,676, Sept. 13, 1929. Threads are made by cutting an unvulcanized sheet which may be produced directly from latex, and vulcanization is then effected (after skeining, if desired). The sheets may be made, from a dispersion prepd. as described in Brit. 290,313 (C. A. 23, 1012), by the method described in Brit. 302,201 (C. A. 23, 4375).

Stiffening and impregnating fibrous materials such as "shoe socks." DUNLOP RUBBER CO., LTD., D. F. TWISS and E. A. MURPHY. Brit. 339,974, June 18, 1929. Shaped cellulosic or other fibrous products such as shoe socks are treated with the foam obtained by whipping up aq. dispersions such as those of rubber which may be prepd. as described in Brit. 332,525 and Brit. 332,526 (C. A. 25, 437), and the treated material is cured and dried or subjected to a setting treatment as described in Brit. 303,544 (C. A. 23, 4596). The material may be preliminarily stiffened, waterproofed and coated with acid latex.

Rubber impregnation of ropes, cords, etc. D. P. FROST and BRITISH ROPES, LTD. Brit. 340,051, Oct. 3, 1929. Some of the yarns to be formed into a strand are treated with an aq. rubber dispersion in such quantity that when the treated yarns, together with untreated yarns, are formed into a strand, the strand will have the desired degree of impregnation. Various details of procedure are described.

Apparatus for manufacture of cords or strings of rubber-impregnated materials, etc. REGINALD TRUESDALE, ROBERT C. SMITH and EDWARD SIMPSON (to Dunlop Rubber Co., Ltd.). U. S. 1,797,249, March 24. Structural features.

Putting rubber tags on laces. A. SCHÖBLER. Brit. 340,173, Feb. 27, 1930. A mixt. of concd. latex and S is applied at the end of a hollow lace, which is pressed into a needle-form in a heated mold (the mixt. being transformed into soft rubber). To accelerate vulcanization, a metal salt or oxide in alk. soln. may be added, with other materials such as tannin, phenol, lampblack, ocher, etc. Various modifications of the procedure also are described.

Pencil erasers. ÉTABLISSEMENTS P. ORANGE ET CIE. Fr. 695,288, May 7, 1930. A rubber suitable for removing pencil marks, etc., contains starchy materials, a suitable compn. being natural rubber 4, starchy substances 10, petrolatum 4, vulcanized waste 2, abrasives 2, factice 1, lithopone 3, S 0.1 and accelerators 0.05 part. The mixt. may be vulcanized or not.

Polymerizing butadiene hydrocarbons. I. G. FARBENIND. A.-G. Fr. 695,299, May 8, 1930. The polymerization of butadiene hydrocarbons using alkali or alk. earth metals is carried out in the presence of small quantities of unsatd. ethers such as vinyl ethyl, vinyl butyl, allyl ethyl or propargyl ethyl ether. Several examples are given. Cf. C. A. 25, 1412.

Polymerizing diolefins. I. G. FARBENIND. A.-G. Fr. 695,441, May 12, 1930. In the polymerization of diolefins by alkali or alk. earth metals, the reaction is carried out in the presence of org. compds. contg. an atom of C, 2 valencies at least of which are satd. with O. Acetals, especially cyclic acetals and among them those contg. a double bond, are particularly advantageous. Several examples are given.

Diolefin polymerization products. I. G. FARBENIND. A.-G. (Georg Ebert and Friedrich A. Fries, inventors). Ger. 520,104, Jan. 26, 1929. The polymerization of butadiene and other diolefins by means of alkali or alk. earth metals is improved and accelerated by addn. of a small quantity of a cyclic diether, e. g., dioxane. The products may be made into filaments or films, which may be hardened by heat or by vulcanization. The vulcanized products resemble soft rubber. Examples are given.

Artificial rubber-like masses. I. G. FARBENIND. A.-G. Fr. 695,300, May 8, 1930. Polyvinyl alcs. are condensed with aldehydes in the presence of catalysts such as $AlCl_3$, $ZnCl_2$ or $NaHSO_4$. The products may be vulcanized to hard substances resembling ebonite.

Synthetic rubber. I. G. FARBENIND. A.-G. Fr. 695,745, May 16, 1930. Masses resembling mixed rubber are made by taking polymerizates, finished or unfinished, of diolefin hydrocarbons and continuing their polymerization with one or more analogous or homologous diolefin hydrocarbons under the same or modified conditions. Examples are given.

Synthetic rubber. I. G. FARBENIND. A.-G. Fr. 696,149, May 27, 1930. Diolefins are polymerized in the presence of alkali or alk. earth metals, their mixts. or alloys in the form of particles of uniform size.

Synthetic rubber. I. G. FARBENIND. A.-G. Brit. 340,008, Aug. 19, 1929. Polymerization of diolefins with alkali or alk. earth metals is effected in the presence of an

org. compd. contg. a C atom with at least 2 valencies satisfied by O, such as satd. and unsatd. acyclic or, preferably, cyclic acetals, or the components of such acetals, *e. g.*, dibutyl acetal, ethylene acetal or other acetals from 1,2- and 1,3-glycols with aldehydes, unsatd. acetals such as those from crotonaldehyde or acrolein and butylene glycol. Various aliphatic, aromatic or hydroaromatic ketones also may be added, as may aldehydes, esters, small quantities of acids such as HOAc or formic acid, etc., and either tough or soft and plastic products can be obtained by varying the proportions of the added substances. The products are *suitable for vulcanizing* or for the *manuf. of coatings, films, lacquers, artificial silk*, etc. Numerous details and modifications of procedure are described.

Synthetic rubber, etc. I. G. FARBENIND. A.-G. Brit. 340,004, Aug. 12, 1929. Unsatd. org. compds. such as acrylic, linoleic, ricinoleic and other long-chain acids or their derivs. such as their esters and their mixts. (*e. g.*, crude linseed oil), unsatd. aliphatic hydrocarbons with more than one double linkage such as butadiene, isoprene or other diolefins or their mixts., or unsatd. aromatic compds. such as styrene, are polymerized in the presence of heavy metal carbonyls such as those of Fe, Ni, Co, Mo, W or Cr. Numerous details and modifications of procedure are described.

Storing unvulcanized rubber sheets. P. BEEBB (to Goodyear Tire & Rubber Co.). Brit. 339,730, Feb. 26, 1929. Adhesion of the sheets is prevented by interposing between their surfaces a non-adhesive liner comprising fabric which has been treated with soap soln. (suitably soap prepd. from coconut oil).

Transparent vulcanized rubber. DOUGLAS F. TWISS and EDWARD A. MURPHY (to Dunlop Rubber Co., Ltd.). U. S. 1,797,250, March 24. Deposits or products are formed directly from a mixt. of rubber latex, S and an ultra-accelerator such as Zn piperidine carbothionolate without use of ZnO, and vulcanized.

Rubber vulcanization accelerators. DUNLOP RUBBER CO., LTD., D. F. TWISS and F. A. JONES. Brit. 340,083, Nov. 1, 1929. Accelerators are prepd. by the interaction of halogen derivs. of C_6H_6 or its homologs with dithiocarbamates. An example is given involving the use of piperidine piperidine-1-carbothionolate and 4-chloro-1,3-dinitrobenzene, and other suitable starting materials also include Zn diethyldithiocarbamate, diethylammoniumdiethyldithiocarbamate and picryl chloride. Various details of procedure are described.

Rubber vulcanization. DEUTSCHE HYDRIERWERKE A.-G. Brit. 339,826, Jan. 8, 1929. Vulcanization is accelerated by the addn. of esters of cyclic alcs. such as the bornyl ester of adipic acid, cyclohexyl esters of hydrophthalic acid, and cyclohexyl ester of benzoic acid.

Vulcanizing synthetic rubber. I. G. FARBENIND. A.-G. Fr. 695,269, May 7, 1930. See Brit. 335,970 (*C. A.* 25, 2022).

Rubber compositions. PAUL HOYER and HANS HOYER. Ger. 522,091, Aug. 25, 1926. A fusible rubber compn. that resumes its original condition on cooling is prepd. by heating rubber or gutta percha with about 20-25% of paraffin, adding S to the melt in the proportion required for vulcanization, and further heating until a liquid of watery consistency is obtained, to which fillers, addnl. rubber and S, etc., may be added. The mixt. should be stirred throughout the process. The product may be cast, or applied to containers as a protective lining. It contains only a little paraffin, the greater part evapg. during the process. An example is given.

Sponge rubber. GUMMI- UND BALATA-WERKE "MATADOR" A.-G. Austrian 122,000, Nov. 15, 1930. Variegated sponge rubber showing marbled or veined effects is prepd. by combining a no. of differently colored rubber masses to each of which suitable softening and gas-forming reagents have been added. The masses may be drawn out into thin sheets and superposed, then rolled up together, twisted and rolled out into strips, which are laid side by side in a mold and vulcanized.

Preventing the deterioration of rubber. THE NAUGATUCK CHEMICAL CO. Fr. 697,630, June 18, 1930. Rubber and other vulcanizable materials are treated with products obtained by the reaction, in the presence of a dehydrating agent, of a secondary aromatic amine having the general formula $R'-NH-R''$ with an acid of the general formula $RCOOH$, in which R is an org. radical or H and R' and R'' are mono- or polycyclic residues, in each of which the C atom *o*- to the N atom is joined to a H atom. Methylacridine obtained by the reaction of Ph_2NH on AcOH, naphthbenzacrindines from phenylnaphthylamine or diacridylethane may be used.

Inhibiting cracking of rubber when exposed to sunlight. SIDNEY M. CADWELL and LUDWIG MEUSER (to Naugatuck Chemical Co.). U. S. 1,798,133, March 31. Sulfoxides (suitably 1-5% the quantity of the rubber) are used such as diphenyl sulfoxide, di-*p*-tolyl sulfoxide, dibenzyl sulfoxide, dibutyl sulfoxide or dibenzyl disulfoxide.

Antioxidant for treatment of rubber. SIDNEY M. CADWELL and SHERMAN I.

STRICKHOUSER (to The Dominion Rubber Co., Ltd.). Can. 310,145, Apr. 7, 1931. Deterioration and surface cracking of rubber are retarded by treating vulcanizable rubber stock with the material obtained by mixing a polyethylenepolyamine b. above 130° and a monohydroxynaphthalene, and then vulcanizing the stock.

Antioxidant for treatment of rubber. CLYDE COLEMAN (to The Dominion Rubber Co., Ltd.). Can. 310,144, Apr. 27, 1931. The deterioration of rubber is retarded by treating rubber in the presence of an accelerator and a vulcanizing agent with 4-4'-diaminodiphenylmethane, and subsequently vulcanizing the rubber.

Regenerated rubber. AMERICAN GLUE CO. Fr. 698,452, July 7, 1930. Rubber is recovered from waste rubber by submitting the waste to the action of the cleavage products from the disocn. of tanned leather during the process of devulcanization.

Plastic materials. JEAN BAER. Fr. 697,641, June 18, 1930. A plastic-elastic material is made by dissolving in CS₂ the polymerization products of halogenated hydrocarbons of the group C_nH_{2n+2} with polysulfides and by mixing this soln. with natural rubber latex. Cf. C. A. 24, 528.

Masses resembling hard rubber. I. G. FARBENIND. A.-G. Fr. 698,298, July 2, 1930. Mixts. of natural rubber and artificial masses resembling rubber are treated in the same way as hardened rubber is usually treated. Besides S, vulcanization accelerators and fillers may be added.

Temperature-regulating system for rubber extrusion apparatus. RALPH B. DAY (to Goodyear Tire & Rubber Co.). U. S. 1,800,180, April 7.

Rubber coatings. DUNLOP RUBBER CO., LTD., and THE ANODE RUBBER CO., LTD. Fr. 697,762, June 21, 1930. Cellulosic or fibrous vessels are coated with rubber or similar vegetable resins applied in the form of solns. or aq. emulsions or dispersions, which may also contain a wax or mixt. of waxes.

Hose of rubber and fibrous material. CHARLES W. LEGUILLON (to B. F. Goodrich Co.). U. S. 1,798,798, March 31. Various details of mech. assembly and vulcanization are described.

Compounding soap-forming materials with other substances. WILLIS A. GIBBONS (to American Rubber Co.). U. S. 1,798,253, March 31. In forming products suitable for compounding with rubber latex, a water-sol. volatile base soap of a higher aliphatic acid such as NH₄ stearate is first mixed with a filler such as C black, in finely divided fluid form, which is nonreactive with the acid, the material is mixed with a rubber latex, and the soap is then reconverted into the original material (suitably by removing NH₃ in a drying operation).

Synthetic rubber. I. G. FARBENIND. A.-G. Ger. 522,090, July 13, 1928. Butadiene hydrocarbons are polymerized by treatment with NaH at atm. or raised temp. An example is given.

Synthetic rubber. I. G. FARBENIND. A.-G. Fr. 697,679, June 19, 1930. In the polymerization of 1,3-butadiene or its homologs or analogs by the aid of alkali metals, the metal is placed in a vessel with one or more walls and is in communication through openings of at least 2 mm. diam. with the hydrocarbon. The vessel used may be filled up with the hydrocarbon which is allowed to polymerize and then added to the main mass of hydrocarbon.

Rubber-vulcanization accelerator. RALPH V. HEUSER (to American Cyanamid Co.). U. S. 1,798,159, March 31. Dibenzylguanidine is used as an accelerator and general mention is made of the use of some similar compds.

Rubber-vulcanization accelerators. THE NAUGATUCK CHEMICAL CO. Fr. 698,259, July 1, 1930. The aliphatic bases produced by the reaction of dihalides of ethylene or its homologs with NH₃ are used as accelerators.

Triazine derivatives containing sulfur. SOC. ANON. POUR L'IND. CHIM. À BÂLE. Fr. 697,599, June 18, 1930. Triazine derivs. contg. at least one atom of exchangeable halogen are condensed with at least one mol. of a S deriv. contg. an SH group and a group easily removed. Such derivs. of S are thiosulfates, thiocyanates, xanthogenates, di- or poly-sulfides. The products are transformed by sapon. and reduction to mercaptotriazines. Examples are given including the prepn. of dimercaptophenylaminotriazine (m. 248°), mercaptoaminophenylaminotriazine (m. 240°), dimercaptonaphthylaminotriazine (m. 260-262°) and mercaptoamino- α -naphthylaminotriazine (m. 257-258°). The products are used in the vulcanization of rubber.

Apparatus for vulcanizing tire and other rubber articles. PAUL WIEGHARDT (to Fr. Krupp Grusonwerk A.-G.). U. S. 1,798,826, March 31. Mech. features.

Vulcanizing rubber. I. G. FARBENIND. A.-G. Fr. 697,568, June 17, 1930. Mixts. of rubbers obtained in different ways from natural and synthetic rubbers are vulcanized in the presence of finely divided C (lampblack). Cf. C. A. 25, 1412.

The World's Rubber Supplies

George Rae

MESSRS. HARRISONS AND CROSFIELD, LTD.

I. Introductory

Until the beginning of the present century, the world's supplies of crude rubber were obtained from trees and shrubs growing naturally in the equatorial regions of the earth, mainly in South and Central America and Central Africa; this rubber is generally known as wild rubber. Today, owing to the rapid increase in the production of cultivated rubber, the output of wild rubber is sufficient to supply only about 3 per cent of the world's requirements.

In 1900 the total output of wild rubber amounted to about 54,000 tons, but this included considerable quantities of moisture and other impurities, and the dry rubber equivalent probably did not exceed 40,000 tons, while plantation output was *nil*. In 1929, the latest year for which complete statistics are available, the output of wild rubber was only 26,000 tons, while the output of cultivated rubber amounted to 821,000 tons. Cultivated or plantation rubber, as it is more generally called, is subdivided into estate and native rubber. Estate rubber is produced on estates owned and managed by Europeans, and on estates over 100 acres owned by Asiatics. Native rubber is produced on holdings under 100 acres. (Some of the larger native holdings in Sumatra and Dutch Bornea may be greater than 100 acres.)

The world production of rubber during 1929 was distributed as follows:

	Tons	Per Cent of Total
Estate: European and American...	414,000	48.9
Asiatic.....	64,000	7.6
Native.....	343,000	40.5
Wild.....	26,000	3.0
	847,000	100.0

II. The Planted Area

Although the seedlings from which the total area under rubber in the East has been developed were planted out in Ceylon in 1876, only about 5000 acres had been planted by the end of 1900. There are two main reasons for this slow rate of growth. The demand for rubber during those years did not appear to be capable of rapid expansion, and much time had necessarily to elapse before it was established not only that the *Hevea Brasiliensis* could be successfully cultivated in the East, but also that of all species of rubber-producing trees it was the most suitable for such cultivation. During the early years of the century the rapid increase in the use of automobiles put a strain on the then existing productive capacity, and under the resulting stimulus of high prices planting proceeded at a rapidly accelerating rate. At the end of 1905, 150,000 acres had been planted, and by the end of 1910, the year of the first rubber boom, the total planted area was about 1,250,000 acres. It amounted to approximately 2,600,000 acres at the end of 1915 and to 4,200,000 acres at the end of 1920. These figures must be looked upon as approximate, as data for the area planted during each year up to 1920 are incomplete and in many cases unreliable.

Since 1920 more information has become available, but some of the published

figures are of doubtful accuracy, and the figures in the acreage table (Table I) must also be looked upon as approximate.

TABLE I
ESTIMATED AREA UNDER RUBBER, DECEMBER 31, 1929
Quantities in Thousands of Acres

Country	Year of Planting								Total
	Up to 1922	1923	1924	1925	1926	1927	1928	1929	
Malaya.....	2,329	45	47	54	102	98	69	46	2,790
Ceylon.....	480	4	5	11	20	13	7	3	543
N. E. I. Estate.....	850	27	44	55	81	109	117	70	1,353
India.....	126	2	1	3	7	13	15	4	171
B. North Borneo....	60	2	4	6	9	9	6	4	100
Sarawak.....	60	5	10	15	20	20	15	5	150
F. Indo-China.....	95	2	3	15	25	30	20	10	200
Siam.....	60	5	5	10	25	20	10	5	140
Others.....	15	10	15	14	6	60
Total (excluding N. E. I. Native)..	4,075	92	119	169	299	327	273	153	5,507
N. E. I. Native ^a	300	..	75	225	225	150	75	25	1,075
^b	450	..	100	300	350	250	150	50	1,650
Grand Total ^a	4,375	92	194	394	524	477	348	178	6,582
^b	4,525	92	219	469	649	577	423	203	7,157

^a Tayler-Stephens (1929). ^b Whitford (1929).

The estimates of the area under native rubber in the Netherlands East Indies, Sarawak, and Siam are, within wide limits, largely guesswork. The only data we have on the native rubber produced in the Netherlands East Indies are the official figures for exports. These exports contain a varying percentage of moisture and other impurities, which is estimated annually by the Dutch officials from samples taken in the various producing districts. By this method the dry rubber content of the total annual exports is calculated, and the figure so arrived at gives an approximation to the actual output. Messrs. Tayler and Stephens, who carried out investigations on behalf of the Rubber Growers' Association, were of opinion that the yield per mature acre was not less than 700 lbs., or not more than 3 acres were required to produce a ton of dry rubber. Others consider that this yield is too high, and that at least 4 acres are required to produce a ton. This explains the difference between the figures for the area planted up to the end of 1922, these figures being estimated solely on the exports and on the opinions about yield per acre. The area planted since that date is usually taken as between two and three times the area planted up to the end of 1922. Most of this area has been planted since the middle of 1924, especially during the years 1925, 1926, and 1927. Owing to the wide divergence in the estimates, the figures for the areas under native rubber in the Netherlands East Indies have been segregated in Table I.

Excluding Dutch native rubber, the total planted area at the end of 1929 amounted to about 5,500,000 acres, of which 3,360,000 acres were on estates owned by Europeans and Americans, 510,000 acres were in Asiatic owned estates over 100 acres, and about 1,630,000 acres were in native holdings under 100 acres.

The proportion of the planted area owned by Asiatics has increased steadily during the last 25 years. Figart, in his report on "The Plantation Rubber Industry in the Middle East" (published by the United States Department of Commerce), estimated that the Asiatic proportion of the total planted area was about

5 per cent in 1905, 20 per cent in 1910, 30 per cent in 1915, and 35 per cent in 1920. At the end of 1925 it was between 45 and 50 per cent, and at the end of 1929 between 50 and 55 per cent; the actual figures for the two years 1925 and 1929 will depend on the estimate adopted for the native rubber in the Netherlands East Indies. Native holdings under 100 acres account for approximately 85 per cent of the total Asiatic owned rubber.

Rubber trees take about five years to reach a tappable size, and are not fully mature till 10 or 12 years old. About 80 per cent of the existing estate rubber trees are tappable. In Malaya and Ceylon 90 per cent of the native rubber is tappable. In the Netherlands East Indies, Sarawak, and Siam, countries for which no reliable data are available, it is generally estimated that less than 50 per cent of the native rubber is tappable.

In considering the relative acreages of estate and native rubber and of mature and immature native rubber, the distinction between estate and native cultivation should be kept clearly in mind. An estate looks forward to continuous or continuously increasing production over a long period of years. It must, therefore, so arrange its cultivation and tapping policy that its reserves of bark are always sufficient for this end, and it carries these reserves of bark largely on the mature areas.

The native has a totally different outlook; he plants from two to four times as many trees to the acre as the European. Upkeep is neglected, little attempt is made to combat disease (unless under compulsion), and his trees are invariably overtopped. He is much more dependent on his immature areas for reserves of bark. An acre of ordinary estate rubber will produce over its productive life a greater quantity than an acre of native rubber, but for the first five or six years of tapping, at least, the native yields per acre will generally be higher.

During the last few years a better knowledge of the effect of various tapping systems, increased cultivation, manuring, establishment of cover crops, terracing, and other methods of conserving the surface soil have increased the yield and probably prolonged the productive life of the estate rubber tree. But by far the most important development has been the planting of high-yielding material by means of grafting a bud from a high-yielding tree on to the seedling of a stock chosen from the point of view of vigorous growth. As in every new development, many difficulties have had to be faced, and the yields from some of the earlier budgrafted areas have proved disappointing; but these difficulties are gradually being overcome. Unfortunately we have no complete data giving the total area planted with budded rubber, but such data as are available indicate that the total budded area is probably not more than five per cent of the total planted area.

III. Output and Exports

The output of rubber in the various producing countries is usually measured by their net exports. With the exception of the output (1) of estates over 100 acres in Malaya, for which we have now monthly figures, (2) of estates in the Netherlands East Indies, and (3) of all rubber in India, for each of which we have annual returns, the exports are the only data published by which output can be measured. In any case they represent accurately the supplies of rubber coming forward each month. Under normal conditions of production, as we shall see later, the stocks in producing countries are not likely to show large variations; net exports will, therefore, be a good approximation to output, and any significant divergence between output and exports will be indicated by the published stock and output figures.

TABLE II
NET EXPORTS OF CRUDE RUBBER, 1910-1930

Year	Netherlands					Plantation			French		Wild		
	British Malaya (1), Tons	East Indies (2), Tons	Ceylon (3), Tons	India (4), Tons	North Borneo (5), Tons	Sarawak (6), Tons	Indo- China (7), Tons	Siam, etc. (8), Tons	Total (9), Tons	South America (10), Tons	Other Wild (11), Tons	Total (12), Tons	Grand Total (13), Tons
1910.....	6,500	2,400	1,600	200	100	10	180	10	11,000	44,000	39,000	83,000	94,000
1911.....	10,800	2,300	3,200	400	100	30	200	70	17,100	43,000	33,000	76,000	93,100
1912.....	20,300	3,700	6,700	700	200	100	250	150	32,100	49,000	31,000	80,000	112,100
1913.....	33,600	6,400	11,400	1,000	500	150	200	150	53,400	43,000	22,000	65,000	118,400
1914.....	47,000	10,400	15,800	1,300	600	300	200	100	75,700	38,000	8,000	46,000	121,700
1915.....	70,200	20,000	20,800	2,200	1,200	600	400	200	115,600	40,000	11,000	51,000	166,600
1916.....	96,000	33,100	24,400	2,800	1,900	1,000	600	300	160,100	38,000	12,000	50,000	210,100
1917.....	129,000	44,000	31,900	4,000	2,400	1,700	900	400	214,300	41,000	12,000	53,000	267,300
1918.....	112,000	42,000	21,100	4,400	2,600	1,500	500	300	184,400	27,000	10,000	37,000	221,400
1919.....	204,000	85,000	44,800	6,600	3,900	2,200	2,900	600	350,000	39,000	9,000	48,000	398,000
1920.....	181,000	80,000	39,000	6,400	4,100	2,200	3,100	800	316,600	30,000	7,000	37,000	353,600
1921.....	151,000	71,000	40,200	5,300	3,200	2,100	3,600	800	277,200	19,000	4,000	23,000	300,200
1922.....	214,000	94,000	47,400	4,900	3,800	3,800	4,500	1,300	373,700	23,000	3,000	26,000	399,700
1923.....	201,000	117,000	37,100	6,400	4,200	5,700	5,100	2,400	378,900	22,000	6,000	28,000	406,900
1924.....	183,000	149,000	37,400	7,700	4,600	6,700	6,500	2,800	397,700	24,000	7,000	31,000	428,700
1925.....	210,000	189,000	45,700	10,100	5,400	9,000	6,300	4,000	479,500	28,000	11,000	39,000	518,500
1926.....	286,000	204,000	58,800	9,900	5,800	10,000	7,400	4,000	585,900	25,000	11,000	36,000	621,900
1927.....	242,000	229,000	55,400	11,300	6,600	11,000	8,000	4,000	567,300	29,000	11,000	40,000	607,300
1928.....	299,000	229,000	58,000	10,800	7,000	11,000	9,000	5,000	628,800	21,000	7,000	28,000	656,800
1929.....	455,500	255,500	80,300	11,700	7,400	11,300	8,700	5,100	835,500	21,100	4,900	26,000	861,500
1930.....	442,700	241,000	75,600	10,800	7,100	10,300	7,600	4,300	799,400	14,300	4,200	18,400	817,800

NOTE.—Most of the figures in this table have been obtained from official sources. The exports of plantation rubber have been adjusted to allow for moisture, etc., in native rubber and for rubber smuggled out of Malaya during the period of regulation of exports.

Table II gives the annual net exports from all the principal producing countries since 1910; the figures for plantation rubber, which include the exports of latex, have been expressed as dry rubber. About two-thirds of the exports during 1929 came from the British Empire and about three-fourths from the British Empire and British controlled estates in foreign countries.

No country except the Netherlands East Indies distinguishes estate rubber from native rubber in its export figures, and although this omission may not be important when considered from the market point of view of the supplies immediately coming forward, it is important to the industry to know approximately what is the proportion of estate to native output in each of the producing countries. Moreover, it is frequently necessary to consider the output of the various producing groups, British, Dutch, etc., and for such discussions we must get beyond the published export figures.

In considering the output of crude rubber, the year 1929 is the only year since 1920 in which normal conditions have more or less prevailed in the producing side of the industry. The output during 1921 was restricted voluntarily, and a considerable amount of both voluntary and involuntary restriction was carried out during 1922. From November 1, 1922, to October 31, 1928, the exports from Malaya and Ceylon were regulated compulsorily, and those from most British estates in the Dutch East Indies were regulated voluntarily in accordance with the Stevenson scheme. Table IIIa shows the distribution of the estimated output during 1929 according to country of production and nationality or race of ownership. The output of the British producers domiciled in the United Kingdom during 1929 was only 28 per cent of the total, and that of British, Dutch, and other European producers was 46 per cent of the total. The output of Asiatic producers was 48 per cent of the total, and most of it was produced on small native holdings. The difficulty of forming an effective voluntary scheme for regulating supplies either among the British producers alone or among all the European producers is obvious.

The difference between the total output (847,300 tons) and the total exports (861,500 tons) is largely accounted for by the export, during the early months of 1929, of rubber which was accumulated previous to the removal of the Stevenson scheme.

The corresponding data for 1930 are given in Table IIIb, and have been influenced considerably by the cessation of tapping which most European and many Asiatic estates practiced during May, 1930, and by the low price of rubber which was maintained during the second half of the year.

The output of rubber is subject to well-marked seasonal variations. In Malaya, Ceylon, the East Coast of Sumatra, and British North Borneo, the period of minimum production (the wintering period) lasts from three to six weeks in the months of February, March, and April. In Java, South Sumatra, and Dutch Borneo it takes place some time during the months of July, August, and September. India has both a spring and an autumn wintering. The months from October to January are the best yielding months everywhere, and the maximum monthly output occurs usually in December. The percentage of the total 1929 output of estate rubber harvested during each month in the principal producing countries is given in Table IV. These figures are all based on the actual crop returns of a large number of estates. The figures for all estates given in the last column give approximately the monthly distribution of the output of *estate* rubber during 1929. No similar data are available for native rubber, but as a larger proportion of it experiences the July-September wintering, the monthly distribution of output would be somewhat different from that of estate rubber.

TABLE IIIb

[illegible]

The yield per acre for estate rubber shows considerable variation from estate to estate, but the average yield for all estates in Malaya, Ceylon, and the Netherlands East Indies during 1929 was approximately 380 lbs. for each acre over six years of age. Native rubber in Malaya yielded 475 lbs. per acre, and the yield of native rubber in the Netherlands East Indies was still higher, the high native yield being entirely due to ample reserves of bark and to the large number of trees per acre. The available data for other countries do not permit of similar calculations being made even approximately, but their average yield per acre, both for estate and native rubber, appears to be less than the figures given above.

The most important factor affecting supplies at the present time is the price of the commodity, which has for several months been below the cost of production. The possibility of a prolonged depression has brought all producers face to face with a very serious situation. As there is very little hope of any combined action by the British and Dutch Governments, each producer must determine his own output policy.

TABLE IV
PERCENTAGE OF THE 1929 ESTATE OUTPUT PRODUCED DURING EACH MONTH

Month	Malaya	Ceylon	Java	Sumatra	All Estates
January.....	9.3	9.1	8.7	9.1	9.1
February.....	6.8	4.4	8.5	7.4	6.9
March.....	7.2	3.0	8.5	6.0	6.8
April.....	7.5	8.3	9.3	6.5	7.8
May.....	8.0	8.4	9.5	7.7	8.2
June.....	8.4	7.3	8.6	8.5	8.2
July.....	8.8	9.5	7.9	9.4	8.7
August.....	8.8	10.4	6.5	9.1	8.6
September.....	8.0	8.6	7.0	8.7	8.1
October.....	9.1	10.5	8.0	9.4	9.2
November.....	8.1	9.8	8.3	8.5	8.5
December.....	10.0	10.7	9.2	9.7	9.9
	100.0	100.0	100.0	100.0	100.0

With regard to estate rubber a number of estates have already closed down, but many consider that they will lose less by producing their maximum crop regardless of the effect of forcing unwanted rubber on the market, although it is probably fair to say that the financial condition of many small estates leaves them no alternative. The more enlightened producers, however, are adopting the policy of tapping only their most productive areas. Some of the largest groups in this country have already commenced to carry out that policy, and their crops during the last three months of 1930 have shown a decline. There can be no doubt of the soundness of such a policy, especially as the total loss is not likely to be seriously in excess of that which would be made by striving after a maximum crop.

With regard to native rubber it is necessary to consider separately the effect of the price on Malayan native rubber from that on Dutch native rubber. The output of Malayan native rubber during 1929 amounted to nearly 200,000 tons—a figure much higher than was indicated either by the assessed standard production of 125,000 tons for the year 1927–1928 or by the actual output of about 100,000 tons during each of the years 1926 and 1928. The output during those two years seemed to confirm the opinion then generally prevalent that the 1927–1928 assessment represented more than these holdings were capable of producing. The output during 1930 is nearly equal to that produced during 1929, and it does not appear to have been affected by the low price, except in so far as this price has probably stimulated abnormally excessive tapping. Recent reports from Malaya, however, indicate that the bark reserves on the small native holdings, which were

built up during the operation of the Stevenson scheme, and which have undoubtedly been an important factor in the high yields obtained during the last two years, are being steadily depleted. As the areas planted in such holdings during the years 1924 to 1928 were comparatively small, a decline in their total output seems probable and the published figures for the last three months of 1930 seem to indicate that the decline may have already commenced. On the other hand, the rubber tree can stand a great deal of heavy tapping and still produce rubber. It seems fairly certain, however, that any decline which may take place in the future output of Malayan native rubber will be almost entirely due to depletion of bark reserves and not to the low price of their product.

The output of native rubber in the Dutch East Indies is in a different category. The natives there have tapped very drastically during the past eight years, but they have large reserves of bark in their immature areas. Their potential output is today much above what is actually being produced, and will increase during the next few years as the areas planted during the years 1924-1928 come into maturity. The decline in the output of Dutch native rubber during the last six months has been largely, though not entirely, due to the disappearance of the market in the relatively inaccessible districts. At the beginning of 1930 most of this rubber appears to have been produced by the owner of the holding and his family, who will tap so long as there is a market. The quantity produced by hired labor was then comparatively small and has now almost disappeared. If the price were to rise to 9d. per pound in London, there is no doubt that there would be a local market for all the rubber that could be produced. The output at this price would be limited by the labor available to harvest the crop. In some of the important native producing districts in the Dutch East Indies the labor locally available is insufficient to harvest all the tappable trees, and labor has to be attracted from other districts, mainly from Java. The laborer normally receives as his wage one-half of what he can produce, although when prices are low he may receive two-thirds or even more. It is possible that the low price of rubber which has obtained during most of 1930 resulted in many laborers leaving the native producing districts, and rubber may have to rise to well over 9d. per pound in London before the labor will return to these districts in adequate numbers to tap all the tappable trees. Tayler and Stephens were of opinion that the potential output of any year would only be attained with rubber at 1s. 6d. per pound.

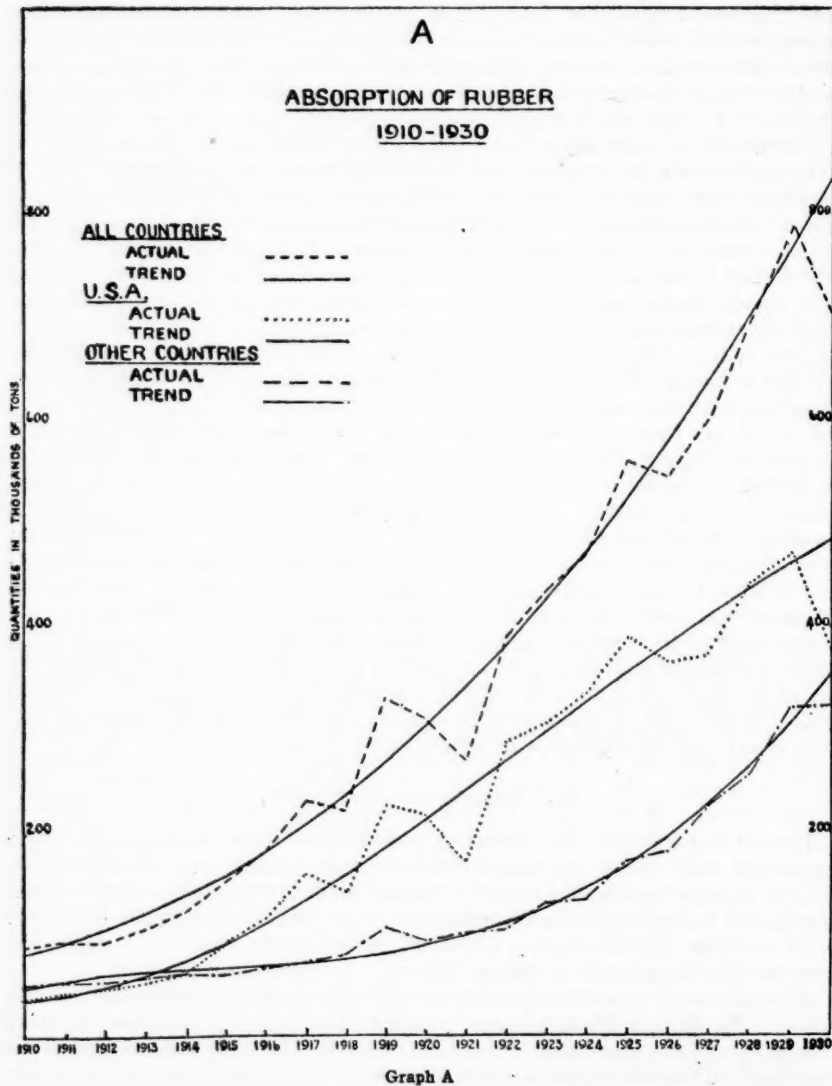
IV. Imports and Absorption

The net imports into manufacturing countries are given in Table V. These figures are, with one or two unimportant exceptions, taken from official returns. France, Japan, Canada, and some of the less important countries include gutta-percha and balata in their crude rubber, but the total so included is negligible. Some countries include reclaim, which at present also appears to be small, but with the increasing trade in reclaim this may become more important.

By absorption is meant the quantity of rubber used in the manufacture of rubber goods. The Rubber Manufacturers' Association of America publishes, monthly and quarterly, the absorption of the United States. No such data are published elsewhere, and we are obliged to use the figures for net imports into other countries as an approximation to their absorption. The net imports into the United Kingdom have to be adjusted for the variations in the stocks in public warehouses in London and Liverpool; an adjustment might be made for variations in similar stocks in other manufacturing countries, but these variations are normally too small to be of much importance. The figures for "other countries" for the years

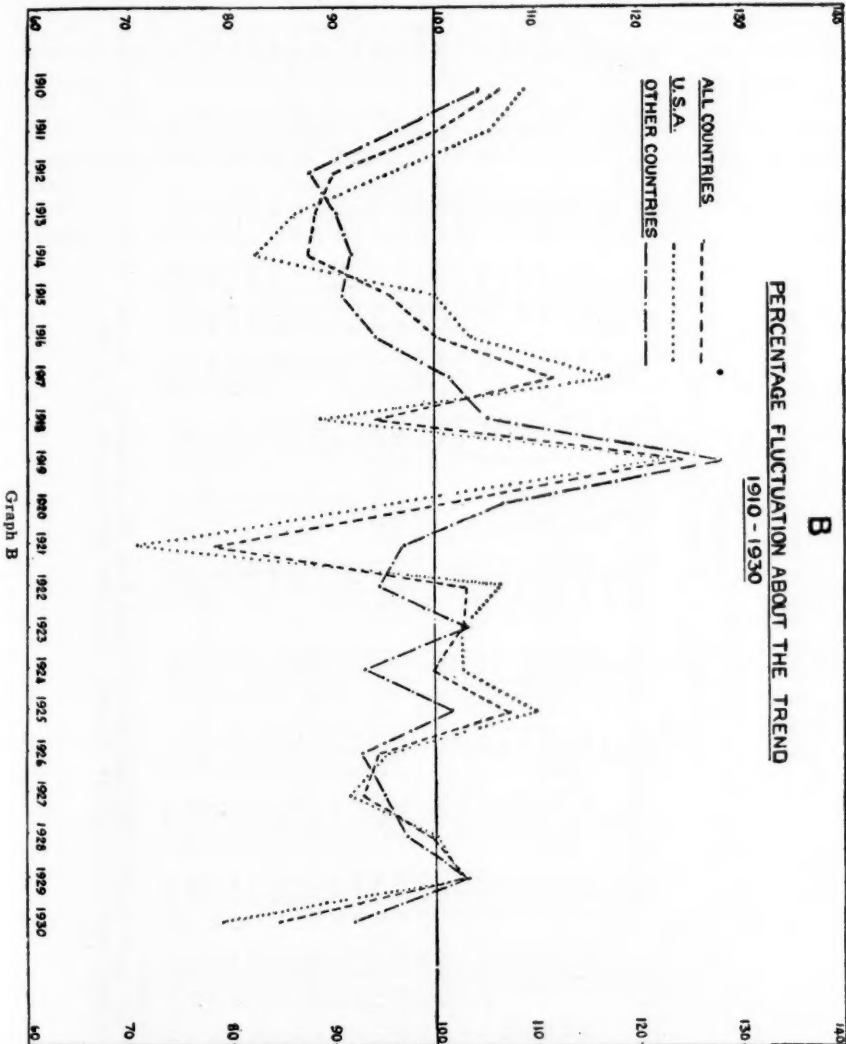
1928 and 1929 have been adjusted to allow for variations of stocks in the hands of manufacturers.

Table VI gives, for the years 1909-1929, the total estimated world absorption, the total absorption in the United States, and the total absorption in other coun-



tries. To each of these series a curve has been fitted and the ordinates of these curves represent the trend values of the absorption for each series throughout the period. These trend values and the percentage which the actual absorption bears to its trend value have also been given in the table. Graph A shows

the actual absorption year by year for each of the groups, together with the trend. If the trend values may be looked upon as "normal" absorption, then this table (and Graph B) indicates for what years the manufacturing industry was running above, and for what years it was below, normal. It is clear from the graph, and



it is indeed obvious without such an analysis that the absorption during 1930, especially in the United States, is well below normal. The fluctuations about the trend for the United States during the past ten years seem to be closely associated with the corresponding fluctuations in general trade conditions. The real consumption of rubber, *i. e.*, the rubber content of rubber goods actually worn out, is un-

TABLE V
NET IMPORTS OF CRUDE RUBBER, 1910-1930

Year	United Kingdom ^a (1), Tons	France ^a (2), Tons	Italy ^a (3), Tons	Germany ^a (4), Tons	Austria and Hungary ^a (5), Tons	Russia ^a (6), Tons	Holland ^a (7), Tons	Belgium ^a (8), Tons	Scandinavia ^a (9), Tons	Spain ^a (10), Tons	United States ^a (11), Tons	Canada ^a (12), Tons	Japan ^a (13), Tons	Australia ^a (14), Tons	Other Countries ^a (15), Tons	Total (16), Tons
1910	20,500	3,800	1,800	13,700	2,000	6,000	1,800	2,200	1,100	400	42,200	1,500	700	400	300	98,400
1911	16,700	5,400	2,400	15,100	2,300	6,000	1,400	2,000	1,300	500	41,900	1,700	900	500	400	98,500
1912	18,700	4,600	3,300	15,400	2,600	7,000	1,400	2,500	1,400	400	56,000	2,500	900	600	400	117,700
1913	25,300	6,500	2,500	16,300	2,800	12,000	2,400	3,600	1,200	600	52,200	2,200	1,200	800	400	130,000
1914	18,500	5,000	2,700	11,000	1,900	11,000	1,800	1,500	1,300	600	62,300	2,500	1,000	1,000	300	122,400
1915	15,100	10,800	5,000	4,000	500	13,000	2,900	2,000	1,000	99,000	4,400	1,700	1,500	400	161,300
1916	26,700	14,700	4,800	2,000	500	9,000	200	1,800	1,700	117,600	4,500	3,000	1,500	500	188,500
1917	26,000	17,000	5,600	1,000	100	5,000	800	1,300	179,300	6,200	3,700	2,000	400	248,400
1918	30,100	18,000	7,100	700	800	143,400	8,300	7,300	3,000	1,100	219,800
1919	42,700	20,100	9,900	4,500	300	2,800	4,000	3,200	3,700	238,400	8,800	10,000	3,500	1,800	353,800
1920	56,800	16,300	6,100	12,600	1,300	100	5,500	3,400	2,300	2,000	249,500	11,900	6,000	3,500	1,300	378,600
1921	42,100	14,800	3,900	21,600	2,400	200	1,000	1,700	1,300	2,200	179,700	8,200	21,000	3,000	1,300	304,400
1922	11,700	27,700	6,400	27,600	2,600	3,100	-3,800	200	1,700	600	296,400	9,400	15,000	2,500	1,800	402,900
1923	12,700	28,600	8,500	18,500	2,600	4,500	800	2,200	2,200	600	301,500	13,200	16,000	2,000	2,900	416,800
1924	-11,600	31,700	8,800	22,700	2,600	1,500	-800	2,700	2,900	900	319,300	14,400	19,700	2,600	3,800	421,200
1925	4,100	34,300	11,400	33,900	2,500	7,500	900	2,900	2,800	1,200	385,600	19,800	12,900	4,500	4,300	528,600
1926	84,900	35,700	9,800	22,800	2,800	7,000	2,700	2,500	3,300	1,100	400,000	20,200	18,300	9,000	4,400	624,500
1927	60,200	35,700	11,300	38,900	3,900	14,000	600	6,500	3,400	1,300	403,500	26,400	20,500	9,500	6,900	642,600
1928	4,800	38,000	12,400	37,900	4,400	8,000	2,200	7,900	3,700	2,100	407,300	30,900	25,800	8,400	9,700	603,500
1929	122,700	61,800	16,400	49,100	4,700	12,700	3,200	9,400	5,500	2,100	528,600	35,500	34,300	15,900	14,700	916,600
1930	120,100	71,400	17,000	45,500	4,000	17,000	2,900	10,700	6,700	2,600	458,500	28,800	32,500	5,000	13,500	836,200

^a Including gutta-percha.

NOTE—Most of the figures in this table have been obtained from official sources. Several of the countries prior to 1914 included re-claimed and scrap rubber among their imports of crude, and a few countries may do so still.

likely to show the same fluctuations as the absorption, and it is probably more approximately represented by the trend. The years when absorption is definitely above the trend would, therefore, represent years when the total stocks of manufactured goods (whether in the hands of manufacturers and dealers or in the form of unused tire mileage on automobiles) are increased. Conversely, when absorption is definitely below the trend, total stocks of manufactured goods are decreased. As the trend does not accurately represent real consumption, the difference between absorption and its corresponding trend value will not, of course, be equal to the rubber content of the fluctuation in the stocks of manufactured goods. It gives, however, a general idea of how these stocks are moving, and this is important in considering stocks of crude rubber, especially in a year like 1930 when the increase in crude stocks is partly counterbalanced by a decrease in the total manufactured stocks as defined above. The rubber content of the decrease in the tire stocks of the United States manufacturers alone during 1930 amounted to nearly 15,000 tons. (Motor transport accounts for approximately 80 per cent of the annual consumption of rubber.)

TABLE VI
ABSORPTION OF CRUDE RUBBER, 1909-1929
Quantities in Thousands of Tons

Year	United States			Other Countries			Total		
	Actual	Trend	Per Cent of Trend	Actual	Trend	Per Cent of Trend	Actual	Trend	Per Cent of Trend
1909	35	33	106.1	45	38	118.4	80	71	112.7
1910	37	34	108.8	48	46	104.3	85	80	106.3
1911	40	38	105.3	50	52	96.2	90	90	100.0
1912	45	47	95.7	50	57	87.7	95	104	91.3
1913	50	58	86.2	55	61	90.2	105	119	88.2
1914	60	73	82.2	60	64	93.7	120	137	87.6
1915	90	91	98.9	60	66	90.9	150	157	95.5
1916	115	111	103.6	65	69	94.2	180	180	100.0
1917	157	134	117.2	73	72	101.4	230	206	111.7
1918	140	158	88.6	80	76	105.3	220	234	94.0
1919	225	184	122.3	105	82	128.0	330	266	124.1
1920	215	212	101.4	95	89	106.7	310	301	103.0
1921	170	240	70.8	100	98	96.9	270	338	78.4
1922	285	268	106.3	105	111	94.6	390	379	102.9
1923	305	297	102.7	130	126	103.2	435	423	102.8
1924	335	326	102.8	135	145	93.1	470	471	99.8
1925	390	355	109.9	170	167	101.8	560	522	107.3
1926	365	383	95.3	180	194	92.8	545	577	94.5
1927	375	409	91.7	225	226	95.1	600	635	92.9
1928	440	435	101.1	255 ^a	262	97.3	695 ^a	697	99.7
1929	470	458	102.6	320 ^a	305	103.3	790 ^a	763	102.9
1930	380	480	79.2	325 ^a	353	92.1	705 ^a	833	84.6

^a Adjusted figure.

Equations to Trends

$$\begin{aligned}
 \text{United States} \quad y &= 184.29 + 26.6553x + .6154x^2 - .05411x^3 \\
 \text{Other Countries} \quad y &= 81.71 + 6.3751x + .8962x^2 + .07003x^3 \\
 \text{All Countries} \quad y &= 266. + 33.0304x + 1.5116x^2 + .01592x^3
 \end{aligned}$$

In each equation x is measured from the year 1919.

It may be thought possible by means of the equation to the trend to predict the absorption during the next few years, but extrapolating beyond the range of observations is a hazardous proceeding. The experience of the next few years may alter the trend and the values calculated today might become progressively more inaccurate. Moreover, in very few of the last twenty years has the trend

value and the actual value coincided so closely as to make the one a good prediction of the other, so that even if the trend values were accurate, the actual absorption during each of the next few years would not necessarily coincide with them.

V. Stocks

The total world stocks of rubber at any particular time may be divided into:

- (1) *Stocks in producing countries.*
- (2) *Quantities afloat to manufacturing countries.*
- (3) *Stocks in manufacturing countries.*

It is needless to say that complete authoritative figures for the stocks in any one of these categories do not exist, but much useful data are published and an examination of these data will indicate the nature of the fluctuations in, and the relative importance of, the various sources of immediately available supplies of rubber.

- (1) *Stocks in producing countries.*

(a) *Stocks on estates.*

The data published by the Malayan Department of Statistics refer to the stocks on estates over 100 acres in Malaya. They include not only the dry rubber on those estates, but also the dry rubber equivalent of all rubber in the course of preparation. Since the beginning of 1930 these data have been practically complete, and the actual quantities, together with the ratio of these quantities to the output of the same estates for the corresponding month, are given in Table VII. The comparatively high ratios during the first four months of 1929 were probably due to the existence of stocks accumulated during the period when the supplies of rubber were officially regulated. But for the twelve months from May, 1929, to April, 1930, inclusive, when conditions were more or less normal, the stocks at the end of each month varied within the comparatively narrow range of from 1.15 to 1.31 months' production, and averaged 1.25 months' production for the whole period. The disturbance to this ratio caused by the cessation of tapping by the majority of estates in May appears to have worked itself out by the end of August, and the ratios for succeeding months are again within the limits noted above. The comparative uniformity in the methods of production among estates in all producing countries in the East would lead to the conclusion that under normal conditions the total estate stocks (including rubber in course of preparation) are likely to be about $1\frac{1}{4}$ months' production, and that any variation in the absolute magnitude of these stocks would be largely due to seasonal variations in production.

TABLE VII
STOCKS ON ESTATES OVER 100 ACRES IN MALAYA AT THE END OF EACH MONTH

1930	Quantity, Tons	Ratio to Output	Corresponding Ratio for 1929
January.....	27,400	1.20	1.45
February.....	24,300	1.31	1.65
March.....	22,200	1.22	1.39
April.....	24,000	1.26	1.37
May.....	12,600	3.40	1.29
June.....	23,000	1.12	1.31
July.....	25,800	1.14	1.26
August.....	26,400	1.11	1.25
September.....	26,600	1.20	1.28
October.....	25,700	1.20	1.17
November.....	26,000	1.21	1.30
December.....	25,800	1.16	1.15

The stocks of rubber on native holdings in Malaya at the end of each month are unknown, but as the native disposes of his product to a local dealer as soon as

it is obtained, these stocks will probably be less than half a month's production, and are likely to show only seasonal variation. Similar conditions are likely to obtain with regard to the stocks of native rubber in the Netherlands East Indies while the price of rubber is steady or is rising, except that the ratio of stocks to monthly output might be rather less than in the case of the Malayan native rubber. When the price is falling, however, the native in the Netherlands East Indies tends to hold up his rubber, and his stocks are likely to increase, at any rate for a time. The stocks of native rubber elsewhere are small.

(b) *Stocks in the hands of up-country dealers in producing countries.*

The only data with regard to these stocks are also published by the Malayan Department of Statistics, and the figures from the beginning of 1929 are given in Table VIII (the published figures for 1929 and the first five months of 1930 have received minor adjustments to allow for stocks in Kelantan, Trengganu, and Perlis). The corresponding stocks in other producing countries are likely to show similar movements to those in Malaya, except perhaps those in the Netherlands East Indies in times of falling prices.

TABLE VIII
STOCKS IN THE HANDS OF UP-COUNTRY DEALERS IN MALAYA AT THE END OF
EACH MONTH

	1929, Tons	1930, Tons
January.....	15,600	17,400
February.....	16,800	17,600
March.....	13,300	17,000
April.....	12,700	15,800
May.....	13,900	14,000
June.....	16,100	13,600
July.....	18,500	15,100
August.....	17,600	15,800
September.....	16,600	16,100
October.....	16,600	15,700
November.....	16,100	18,000
December.....	17,000	18,700

As in the case of estate stocks, these up-country dealers' stocks have not shown much fluctuations beyond what may be expected from seasonal variations in production.

(c) *The stocks in the hands of dealers at the ports of shipment.*

The available data are given in Table IX. The Malayan Department of Statistics publishes at the end of each month the stocks in Singapore and Penang. They also publish monthly the "Ports Stocks," i. e., the quantities of rubber afloat in the harbors and held by the Harbor Boards of Singapore and Penang. The Colombo Rubber Traders' Association publishes the stocks of its members at the end of each quarter. Their figures include all the rubber in Colombo, with the exception of a relatively small quantity of native rubber.

There are no data for corresponding stocks elsewhere in the East. The monthly stocks in Brazil (Para and Manaus) are also given in Table IX.

For more convenient reference, the total of the declared stocks in Malaya at the end of each month during 1930 have been collected in Table X; the cessation of tapping during May is reflected in the May and June figures. The activity of the remilling factories in Singapore, where about 80 per cent of the Dutch native rubber is prepared for the world market, is a factor of some importance in the Singapore stocks.

TABLE IX
STOCKS AT CERTAIN PORTS OF SHIPMENT

	Singapore		Penang		Ports ^a	Colombo		Para and Manaos	
	1929, Tons	1930, Tons	1929, Tons	1930, Tons	1930, Tons	1929, Tons	1930, Tons	1929, Tons	1930, Tons
January.....	24,800	28,500	4,800	5,000	6,300	4,400	3,700
February....	27,200	32,100	5,200	5,500	6,800	5,000	4,400
March.....	25,300	32,600	4,100	5,500	5,100	4,600	4,800	4,300	4,600
April.....	22,600	34,000	3,800	5,600	6,100	4,700	4,500
May.....	26,300	33,300	4,500	5,300	3,800	4,400	4,400
June.....	24,900	31,500	5,500	4,500	4,300	5,300	3,900	5,100	4,600
July.....	28,500	31,800	5,400	5,100	6,000	4,400	4,700
August.....	25,200	33,400	5,600	6,200	5,900	4,400	4,500
September...	27,100	29,000	5,000	5,300	6,800	5,700	5,800	4,500	4,900
October.....	28,100	28,300	5,600	4,200	4,700	3,800	5,200
November...	25,400	29,800	4,400	4,400	4,000	3,800	4,500
December...	27,900	32,200	5,200	4,600	5,600	5,600	5,200	3,800	5,300

^a Quantities of rubber afloat in the harbors or held by the Harbor Boards in Singapore and Penang.

TABLE X
DECLARED STOCKS IN MALAYA AT THE END OF EACH MONTH DURING 1930

	Malaya, Tons
January.....	84,500
February.....	86,300
March.....	82,400
April.....	85,500
May.....	68,900
June.....	76,800
July.....	83,800
August.....	87,600
September.....	83,900
October.....	78,600
November.....	82,200
December.....	86,900

(d) *Quantities in transit within and between producing countries.*

There are no published data for such rubber, but their monthly fluctuations are likely to be small.

The general conclusions which may be drawn from the discussion of stocks in producing countries since the middle of 1929 are: (1) that they represent only working stocks, and their total is determined mainly by the rate of production; (2) that under normal conditions of production their fluctuations from month to month are largely influenced by seasonal variations in output; and (3) that their monthly fluctuations are not normally an important factor in the fluctuation of total world stocks. The importance which the market attaches at present to the Malayan stock figures is due to the indications they give of the output of Malayan native rubber.

(2) *The quantities afloat to manufacturing countries.*

By quantities afloat is meant rubber which has been declared as an export but has not yet been declared as an import. They will, of course, include rubber in transit between manufacturing countries although these quantities will generally be small compared with the quantities in transit from producing countries. There are no means of determining these quantities accurately, but as they are mainly dependent on the rate of exports from producing countries and the time which elapses between the two declarations, an approximate estimate of the quantities

afloat at the end of any month might be taken as the total exports from producing to manufacturing countries during that month, together with from one-fourth to one-half the corresponding exports during the previous month. The most important source of fluctuation in the quantities afloat, under normal conditions of production, is the seasonal variation in exports, which in turn depends on the seasonal variation in output. The quantities afloat will, therefore, be at their maximum about January and at their minimum about April. The difference between the maximum and minimum will probably be between 15,000 and 20,000 tons.

(3) *Stocks in manufacturing countries.*

These consist of stocks in warehouses at the principal ports and stocks in the hands of manufacturers. They may be conveniently considered together, for, with the exception of the United States, no country publishes the stocks of crude rubber in the hands of manufacturers, and, in discussing the stocks in the United States, it is the total stocks of manufacturers and dealers that are usually considered. It is, however, important to bear in mind that the stocks in the hands of United States manufacturers have generally been from 60 to 80 per cent of the total United States stocks.

Table XI gives the stocks at the end of each month, since the beginning of 1929, in London, Liverpool, Amsterdam, Hamburg, and the United States. The United States figures are obtained by comparing the monthly official figures for net imports with the monthly absorption (brought up to 100 per cent) as reported by the Rubber Manufacturers' Association. In arriving at these figures, the official census of the total stocks at the end of 1929, 122,100 tons, has been taken as the starting point.

TABLE XI
STOCKS IN CERTAIN MANUFACTURING COUNTRIES AT THE END OF EACH MONTH

1929	London, Tons	Liverpool, Tons	Amsterdam, Tons	Hamburg, Tons	United States, Tons	Total Tons
January.....	25,200	3,800	1,300	5,900	76,200	112,400
February.....	25,600	4,100	1,100	5,100	95,700	131,600
March.....	28,200	4,300	900	8,900	97,200	139,500
April.....	31,400	4,600	900	5,400	101,900	144,200
May.....	31,300	4,500	1,300	4,000	101,000	142,100
June.....	31,000	4,600	1,600	3,600	96,300	137,100
July.....	30,100	4,700	1,600	4,300	95,700	136,400
August.....	35,600	7,500	1,900	5,600	92,700	143,300
September...	42,200	10,000	2,200	4,100	90,700	149,200
October.....	47,800	13,900	2,200	4,100	91,800	159,800
November...	52,500	17,700	2,200	4,200	105,100	181,700
December....	54,300	18,900	2,200	3,200	122,100	200,700
1930						
January.....	60,400	19,800	2,100	5,500	130,300	218,100
February.....	64,600	20,600	2,200	3,000	138,400	228,800
March.....	68,900	21,100	2,200	5,600	144,700	242,500
April.....	74,700	23,800	2,200	3,700	147,500	251,900
May.....	77,300	25,400	2,300	4,300	148,100	257,400
June.....	80,300	27,300	2,300	2,900	150,900	263,700
July.....	81,000	28,300	2,300	2,300	153,800	267,700
August.....	80,900	29,700	2,200	3,300	157,700	273,800
September...	83,300	34,700	2,300	5,000 ^a	166,800	292,100
October.....	77,600	38,800	2,400 ^a	5,000 ^a	183,900	307,700
November...	76,900	39,700	2,400 ^a	6,000 ^a	188,900	313,900
December....	78,000	40,500	2,400 ^a	6,000 ^a	202,600	329,500

^a Estimated.

The fluctuations in the stocks in the East and in the quantities afloat are normally the result of variations, mainly seasonal, in production, and in time these fluctuations are translated to the United Kingdom and the United States—the period of minimum arrivals nearly coinciding with the period when manufacturing activity is normally approaching its maximum. The purely seasonal variations in the stocks in the United Kingdom and United States will thus be of greater amplitude than those either in producing countries or in the quantities afloat—a point of considerable importance when world stocks are low.

But apart from these purely seasonal movements, and at present greatly overshadowing them, there is the movement in the stocks due to the excess of annual production over annual absorption. This movement is almost entirely confined to the stocks in London and Liverpool and in the United States. Surplus rubber is more easily financed in these countries, especially in the United Kingdom, and it deteriorates if kept too long in the East. Furthermore, any variation in the working stocks held by manufacturers outside the United States will be reflected in the stocks in London and Liverpool, which in addition act as the main reservoir of immediately available supplies, and have accordingly shown large fluctuations during the past twenty years.

I have not discussed any figures earlier than 1929 (1) because they have become more complete since that date, and (2) because for the six years previous to 1929 the operation of the scheme regulating the supplies of rubber lessened the normal significance of these figures.

Finally, with regard to stock data generally, the figures for total world stocks, even if they could be obtained accurately, are meaningless unless they are compared with the rate of absorption. The ratio of the total crude stocks (declared and undeclared) at the end of any month to the absorption during that month has shown great fluctuations, part of which are seasonal. During the last two years alone it has varied between $5\frac{1}{2}$ and 11; and has shown even greater fluctuation in the past. The question as to what constitutes a "normal" stock does not admit of any simple answer. It will depend on the time taken to prepare and deliver the rubber, on the stocks held by producers, manufacturers, and dealers to provide against unforeseen interference with its progress from the estate to the factory, on the relation of production to absorption and of absorption to real consumption, and on the season of the year. Time does not permit me to discuss these factors, but it seems to be generally accepted that a total world stock of crude rubber equivalent to roughly six months' absorption is necessary for the smooth working of the industry.

The Evaluation of Raw Rubber

G. Martin

The purchase of supplies for a rubber factory often involves a decision as to the relative merits of different samples of raw rubber. In view of the variety of needs the method of arriving at a decision must be left to the wisdom of the technical staffs concerned; but when a large portion of the output from the East is involved, affecting producers and manufacturers everywhere, it is desirable to discuss fully the methods employed to ensure that the final decision is as wise as its importance warrants.

A problem affecting the whole of the rubber industry has now arisen in the East in connection with the preparation of smoked sheet. Firewood for smoking is becoming more difficult to obtain, and already some estates have been compelled to consider the production of an alternative form of rubber. As the Tropics become more cultivated, the acuteness of the problem will increase, and unless some change in the method of production occurs, sheet will tend to be replaced by crepe. It is presumed that there is a demand for sheet apart from crepe and that each form of rubber serves a purpose which the other cannot fulfil; but there is no clear and authoritative indication from manufacturers as to the differences which make both forms of rubber essential. It is of interest to point out that apart from form, color, odor, and reaction to swelling agents, there is no test which would distinguish between high grade sheet and crepe rubber unless both are prepared from the same latex, in which case sheet has a slightly higher content of mineral matter (*Bull. Imp. Inst.*, 21, 303 (1923)) and a greater tendency to absorb moisture from the atmosphere (de Vries, "Estate Rubber," 1920, p. 340), and possibly better aging properties (Martin, *Trans. Inst. Rubber Industry* 2, 354 (1927)). It is not proposed to discuss the relative merits of sheet and crepe although the subject is an illustration of the difficulty of evaluating raw rubber so as to obtain results which are in agreement with the ideas and experience permeating the industry. To the planter there appears to be a demand for sheet as well as for crepe, and he purposes to meet that demand if it is at all possible.

The problem the planter (and the manufacturer) has to face is whether it is necessary to dry sheet in smoke to obtain rubber of as good a quality as that now supplied.

Samples of rubber have been examined, dried in air, in comparison with those dried in smoke, and it is proposed to discuss the various tests which have been and which might have been applied, and the interpretation of the results obtained, not with a view to comparing the properties of the two forms of rubber, but because the same problems arise in connection with the evaluation of rubber for general purposes, irrespective of the type of rubber.

The ultimate criterion of the relative values of sheet dried in smoke or any other medium is the ease with which it can be handled, and the service it renders when converted into manufactured articles. This is the practical test, but it is too slow, and requires very careful planning to obtain reliable results.

The chemist is accustomed to carrying out accurate experiments in test tubes, and he may not always realize the amount of error attached to experiments on a works scale and how difficult it is to avoid the possibility of a misleading result.

In the plantation industry it is recognized that single or even duplicate experiments are of little value in determining the effect of modifications of agricultural

operations. It is first necessary to determine the error in a number of replications of the control, then to decide what is the smallest difference which it is desired to detect between the control and its modifications, then to calculate the number of experiments necessary to give a significant result, and after that to carry out the necessary experiments. It may not be convenient to do this, but without it the works test is of little value.

For example, two samples of rubber were recently submitted by the Ceylon Rubber Research Scheme to three manufacturers for a report on color when made into a certain class of manufactured article. One manufacturer reported that the goods from A were paler than those from B, another that those from B were paler than those from A, and the third that they both gave articles of the same color. Even though each manufacturer had obtained the same results, there is a reasonable possibility that this result might be accidental and contrary to general experience. In order to obtain a reliable result, it would have been necessary for each manufacturer to determine from as many experiments as possible the standard deviation in color of the average for each sample, and then whether the difference between the two averages is in excess of a well-known mathematical factor calculated from the two standard deviations.

Such methods of examining rubber are usually too complicated, and therefore it is necessary to rely upon laboratory tests to determine the relative merits of different samples. It must not be concluded, however, that the works test is without value. The works test may be useful in determining whether there are indications of pronounced abnormalities which have escaped observation in the laboratory. For example, sheet not dried in smoke might quickly lose its tackiness after calendering or tend to extrude irregularly, or prove difficult to mix with certain ingredients. It is impracticable to test for every possible abnormality in the laboratory, and a works test may indicate that special laboratory tests are required in addition to those usually carried out. There is no doubt that works tests are desirable before attempting the large scale production of any new type of rubber, but they can only be used to indicate abnormality. They cannot be used to evaluate the rubber unless carried out on an elaborate scale.

The first laboratory tests to consider in connection with the evaluation of raw rubber are those relating to its manipulation in the factory. These include cleanliness, mastication, mixing, calendering, extruding and moulding properties, tackiness, liability to scorch, etc.

Cleanliness hardly comes within the scope of laboratory tests, as the bulk of plantation rubber is clean, and the detection of dirt only requires a superficial examination. It pays the planter to keep his rubber as clean as possible, because dirt at any stage of preparation leads to defects which affect the market price of his product, *e. g.*, dirty latex encourages fermentation and bubbles, dirty machines cause streaks and discoloration, and so on.

As regards the cleanliness of an alternative form of rubber to smoked sheet, there are two points of interest, *viz.*, sheet dried without smoke avoids the risk of contamination by tarry deposits in the smoke house, and in the absence of darkening agents would have a pale color which would easily reveal the presence of dirt.

Nearly all the properties of rubber which affect ease of handling are connected with plasticity and elasticity. Several methods are used for the measurement of plasticity. It is impossible to discuss in detail within the limits of this paper their relative merits, but a few observations on more important points may be helpful in connection with the evaluation of raw rubber.

Plasticity.—The plasticity of a solid is not a definite or simple property like the

viscosity or fluidity of liquids. When the deforming force is small there is no permanent flow and the apparent plasticity of the rubber is nil. As the deforming force increases, so does the apparent plasticity of the rubber. The mathematical relation between deforming force and apparent plasticity is not known. Consequently a comparison of plasticities under a fixed load is valid only for that load. This is illustrated in Table I, which shows the rate of extrusion of different samples of masticated rubber at two loads, the lower one being similar to that chosen by Marzetti (*Giorn. chim. ind. applicata*, July, 1923) of the Pirelli Rubber Co. for his tests, and the higher one similar to that selected by Griffiths (*Trans. Inst. Rubber Industry* 1, 308 (1926)) of the Dunlop Rubber Co. for his.

TABLE I
RATE OF EXTRUSION AT 85° C.

Sample No.	Load 165 Lbs./Sq. In.	Load 1000 Lbs./Sq. In.
	Cc./Hour	Cc./Minute
1380	25.6	28.6
1381	23.8	27.5
1382	15.4	26.6
1383	14.9	24.8
1384	14.5	24.8

Marzetti studied the relation between load and rate of deformation of rubber but the range of loads was small. In Fig. 1 is shown the relation between load and rate of deformation of masticated rubber over a much wider range of loads

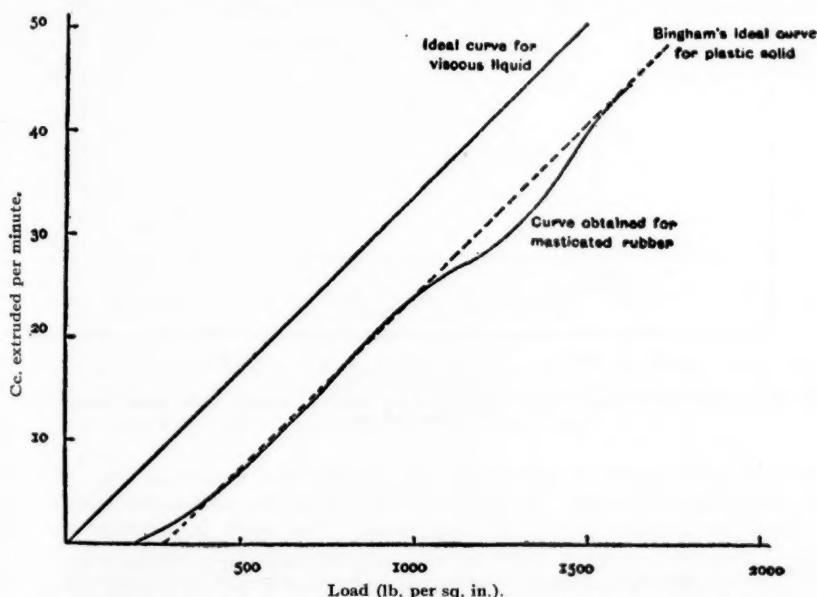


Figure 1—Extrusion of Masticated Rubber. Relation between Load and Rate of Flow

as determined by extrusion through a narrow orifice. The curve is similar in shape to that which Bingham ("Fluidity and Plasticity," 1922, p. 217) regards as typical for plastic substances in general and which is also shown in Fig. 1. Bingham's work was mostly carried out on paints, and from the shape of the load-rate of deformation curve he deduced that plasticity was made up of two inde-

pendent properties which he called mobility and yield value. Mobility refers to the steep straight portion of the curve and yield value to the intercept along the load axis. These ideas have not met with general approval but this would not be of importance if they enabled comparisons of plasticity to be made irrespective of the conditions of the test. Unfortunately this is not possible in the case of rubber because, in spite of the similarity between Bingham's ideal curve and the actual curve for masticated rubber, there are important anomalies and, in addition, it is difficult to measure with accuracy the rate of flow of rubber under high loads. For this reason the curves shown in Fig. 1 cannot be regarded as evidence either for or against Bingham's ideas. They merely emphasize that the methods used for the measurement of the plasticity of rubber do not lead to results to which Bingham's treatment can be applied.

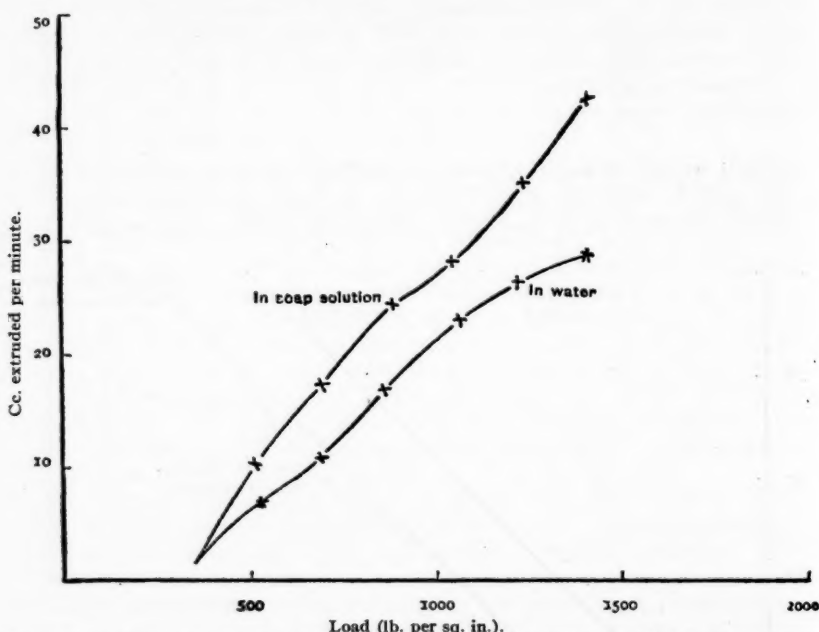


Figure 2—Relation between Load and Rate of Extrusion of Masticated Rubber Illustrating the Effect of Slip

The irregular results at high loads are probably due to surface slip. In the case of the extrusion tests, the orifice and the rubber are surrounded with water to obtain an accurate control of temperature. This tends to increased surface slip. Under low loads the extruded worm is smooth, under higher loads corrugated, and at the highest loads extrusion occurs in a series of jerks corresponding with white patches where moisture has penetrated the rubber.

If a little soap or alkali is added to the water surrounding the orifice, extrusion occurs more quickly at all loads, suggesting that the amount of slip has increased (see Fig. 2).

In the Williams test, slip is not so likely to occur, because the rubber is held between pieces of paper which tend to prevent the surface layers from moving. According to Garner (*India Rubber J.*, 78, 20 (1929)), however, when masticated

rubber is smeared with graphite (which would tend to increase slip) it appears to be nearly ten times as plastic as the same rubber smeared with carbon black. It is desirable that further particulars of this experiment should be given, as it has not been possible to confirm Garner's results. Smearing masticated rubber with graphite, French chalk, or carbon black was found to have little effect on the results of plasticity tests in the Williams press.

An interesting modification of the Williams test was introduced by van Rossem ("Plasticity and Elasticity of Rubber," Sept., 1927). In the Williams test, a ball of rubber is compressed under a weight, and as the rubber decreases in thickness the area of contact between rubber and weight increases, and so the load per unit of area decreases. Van Rossem introduced a disc of known area between the rubber and the weight, so that the load per unit of area remained constant. The conditions are now comparable to two discs, one vertically over the other, the lower one fixed, and the top one free to move in a viscous liquid. From the rate at which

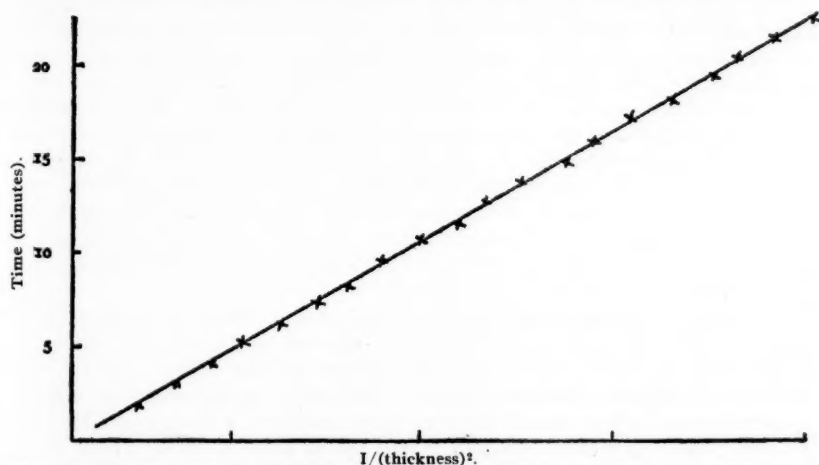


Figure 3—Relation between Thickness of Masticated Rubber and Time of Compression (van Rossem Method) at 70° C.

the top disc moves to meet the lower one, the viscosity of the liquid can be calculated. According to Taylor ("Bakerian Lecture to the Royal Society," Vol. 108, 12), the equation governing the motion of the top disc is

$$\frac{\frac{1}{S^2} - \frac{1}{S_0^2}}{t} = \frac{4}{3} \frac{mg}{\eta \pi a^4}$$

where S_0 and S are the distances between the discs at the beginning and end of the time interval, t , mg is the downward force operating on the top disc, a is the diameter of the discs, and η is the viscosity of the fluid.

When carrying out a test, all the values on the right-hand side of the equation remain constant and therefore

$$\frac{\frac{1}{S^2} - \frac{1}{S_0^2}}{t} \text{ is constant.}$$

Van Rossem has given detailed thickness and time readings for masticated rubber compressed by a loaded disc at different temperatures. The highest temperature for which his results are given is 70° C., at which temperature the plastic properties predominate. Taking the values given and plotting t against $\frac{1}{S^2}$, the straight line shown in Fig. 3 is obtained, showing that $\frac{1}{S^2}$ is proportional to t , in agreement with

Taylor's equation. This result has been confirmed at 100° C., but heavy loads resulting in rapid displacement of the rubber tend to cause slipping, and give rise to irregular results.

It follows from this that the time required to compress different samples of rubber from one fixed thickness to another is directly proportional to the apparent viscosities of these samples under the load and temperature conditions chosen, and experience with hundreds of extrusion and compression tests confirm this. The same reasoning also shows that the time taken in the Williams test to compress different samples of rubber from one known thickness to another is directly proportional to the apparent viscosities of the samples. There are therefore three methods available for measuring the apparent viscosity of rubber in units which are directly proportional to one another and to absolute units. The compression methods are preferred to the extrusion methods because they are more convenient and probably more accurate. Of the two compression methods the Williams test is preferred to the van Rossem modification, because the results are proportional to the average viscosity over a wide range of loads, and not to a single viscosity at an arbitrary load. *The results must of course be in terms of the time interval between two fixed thicknesses, and not as is more usual in terms of the final thickness after a fixed time interval.*

A determination of the plasticity of raw rubber is of value for the purpose of evaluation only if it bears a relation to the behavior of rubber on mastication. A considerable amount of evidence on this subject is being collected by the staff of the Ceylon Rubber Research Scheme. The results so far obtained indicate that a hard, raw rubber usually requires more mastication than a soft one, and *vice versa*. The correlation coefficient is 0.63 for 36 pairs of tests. If the correlation were perfect, this figure would be 1.0, and if there were no correlation it would approach zero. In view of the large number of tests, the correlation is significant, but it is not so good that the amount of mastication required can be predicted from the hardness of the raw material. It is necessary, therefore, when evaluating raw rubber to carry out a mastication test. For this purpose the conditions must be standardized as accurately as possible, otherwise the results will be unreliable.

Having fixed the conditions of mastication, it is necessary to decide whether for the purpose of evaluation the rubber shall be masticated for a definite period, and the result of the test expressed in terms of plasticity, or whether the rubber shall be masticated until it reaches a definite plasticity, and the results expressed in terms of the amount of mastication required. The latter is preferable because the results are in units which have a practical value, and which are easily understood without familiarity with laboratory operations. In the case of the laboratory of the Ceylon Rubber Research Scheme, the results of mastication tests represent the amount of mastication required to reach the average plasticity of sixteen samples of masticated rubber supplied by six different rubber manufacturers, after mastication to the plastic condition most useful for their purpose. The difference between the masticated samples was enormous, some manufacturers

apparently preferring rubber forty times as plastic as others. If the condition of the hardest rubber is reached in ten minutes on the laboratory rolls, it would require ninety minutes to reach the condition of the softest.

It is found that an average sample of raw rubber must be passed through the laboratory rolls about 100 times under the conditions selected by the Ceylon Rubber Research Scheme to reach the average plastic condition required by manufacturers. Some samples require as few as 80 passes and some as many as 120 to reach this condition, but it is very exceptional to find a sample outside this range.

When carrying out tests on small laboratory rolls it is not practicable to remove small portions of rubber to determine when the required plasticity is reached. It is only necessary, however, to determine the plasticity of the rubber at two stages of mastication, preferably near to that giving the plasticity required. From the results, a simple calculation enables the amount of mastication required to be calculated. The reason for this is that within wide limits equal increments in mastication cause equal increments in plasticity. This is not obvious from the usual mastication-plasticity curves, because the results are plotted in time units (which correspond to viscosity) instead of their reciprocal volume units (which correspond to fluidity). Bingham (*loc. cit.*, p. 81) has previously pointed out

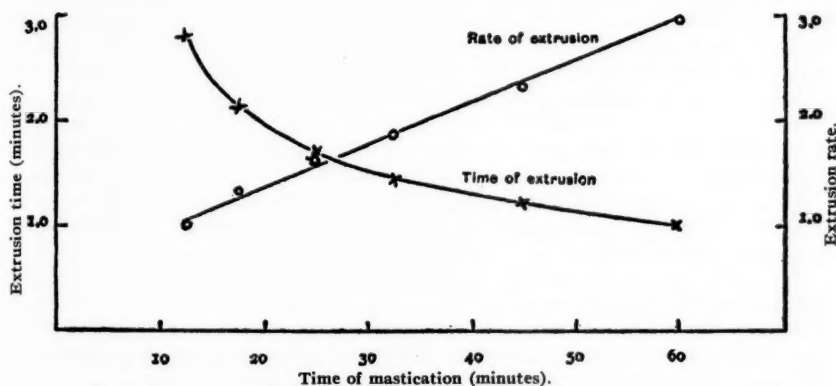


Figure 4—Mastication—Plasticity

that when viscosities are not additive, fluidities sometimes are. When Griffiths' figures (*loc. cit.*) for the time of extrusion are converted into their reciprocal values which are proportional to rate of extrusion and plotted against time of mastication, the straight line shown in Fig. 4 is obtained instead of the usual hyperbolic curve. Similarly when Porritt and Fry's (*Trans. Inst. Rubber Industry*, 3, 205 (1927)) figures for solution viscosity, after different periods of mastication, are converted into their reciprocal fluidity values and then plotted against mastication, the relation is almost a linear one. For this reason it is preferable to express plasticities as rate of flow instead of as time of flow, and this principle should be used whether the compression or the extrusion method is employed. This method also has the advantage that a high figure corresponds to high plasticity, and a low figure to low plasticity.

Although the technic of plasticity tests involves considerable academic discussion, the method finally adopted by the Ceylon Rubber Research Scheme for the purpose of evaluation is simple, and the results are easily understood without academic knowledge. It is open to criticism chiefly because conditions of testing

affect the differences between samples of rubber. Care has been taken, however, to secure average conditions whenever possible, and the results should undoubtedly be useful for the evaluation of rubber for general purposes.

It is found that sheet which is not dried in smoke requires on an average 121 passes through the laboratory rolls to reach the required plasticity, compared with 106 for smoked sheet from the same latex. According to these tests air-dried sheet requires about 15 per cent more mastication than smoked sheet. This figure will of course vary with the conditions of testing, though any reasonable system of testing will probably indicate that smoked sheet is more plastic than air-dried sheet.

Elasticity.—The elastic deformation of raw and masticated rubber has not received the same attention as plastic deformation. Nothing is known of the fundamental principles, and the methods of measurement so far adopted are very arbitrary. They are probably useful for works control, but are not likely to lead to useful results in the evaluation of raw rubber. Experience shows that plastic deformation is always accompanied by elastic deformation, and the more rapid the deformation, the larger is the elastic deformation. Methods of measuring the plasticity of rubber by determining the final thickness as employed in the more usual form of the Williams test give a result which represents the total flow due to both plastic and elastic deformation. On the other hand, measurement of the rate of flow as recommended in this paper may involve only plastic flow, as the rubber probably remains in the same state of elastic tension throughout the test.

Rate of Vulcanization.—Vulcanization tests were among the first to be applied to the evaluation of raw rubber. For various reasons pure mixings soon obtained a popularity which, however, has decreased with the lapse of years. At one time the rubber-sulfur mixing was used almost exclusively for evaluation purposes, but the author has strong evidence from private information that most manufacturers are now of opinion that the rubber-sulfur mixture is of limited value for the evaluation of rubber.

There are three major research organizations maintained on behalf of the planters which deal with the evaluation of large quantities of raw rubber, one in Malaya, another in Java, and a third in Ceylon. All three have practically identical plants for carrying out vulcanization tests, and yet they employ mixings containing different proportions of rubber and sulfur, different temperatures of vulcanization, and different standards of vulcanization. Consequently it is necessary to be familiar with the details of the methods employed, and the average results obtained before an individual result can be of value to the bulk of technologists. There would be no objection to this if it led to a more detailed knowledge of the behavior of rubber under different testing conditions, but the evidence of experience is against this point of view. Attempts are now being made to standardize the procedure of the three organizations. In this connection British manufacturers have rendered considerable help through their Research Association.

The importance of standardizing conditions when carrying out vulcanization tests has been strongly emphasized in America as a result of a joint investigation by a number of commercial concerns (*Ind. Eng. Chem.*, 20, 1245 (1928)). The results of the joint investigation are of considerable value, but do not necessarily apply to British conditions, principally because the Schopper ring testing machine is in general use throughout Europe and the Scott strip testing machine throughout America. There is scope for similar work by British manufacturers using the Schopper ring testing machine, and there is no doubt that the planters' research organizations would be pleased to coöperate if such an investigation were undertaken.

The object of a vulcanization test is to determine the rate of vulcanization and the strength of the rubber when vulcanized. Both have a practical value in so far as they serve to detect abnormalities. For this reason the average rate of vulcanization is of importance, and when evaluating raw rubber for general purposes, it is assumed that either quick or slow curing material is inferior. It is presumed therefore that the rubber which is to take the place of smoked sheet should have the same rate of vulcanization as smoked sheet. This is difficult to achieve without additions to the latex or special modifications of the methods of preparation as smoke constituents, absorbed by the rubber and deposited in it, retard the rate of vulcanization, and air-dried sheet prepared in exactly the same way as smoked sheet is bound to vulcanize more quickly. This is probably not serious when marketing a new type of rubber which is easily distinguished from other types. Uniformity within the type is understood to be of more importance than a few minutes more or less in the average rate of vulcanization.

Experience soon teaches one the dangers of attaching too much importance to tensile strength determinations. The total range of variation is within about 20 per cent for carefully prepared rubber, and accidental differences in procedure may occasionally reverse the position of samples which occupy extreme positions. Moreover samples which are comparatively weak in a rubber-sulfur mixing soon after vulcanization may be relatively strong on aging or when vulcanized in another mixing. There is no doubt that more than one experiment is necessary to establish with certainty the usual difference in the strength of different samples of plantation rubber. This question must be studied along statistical lines to determine the reliability of the usual differences between samples of rubber.

It has been the practice in some quarters to evaluate rubber merely on the results of vulcanization tests in a rubber-sulfur mixing. It must be realized, however, that as a test it has its limitations. Its chief value lies in the fact that, combined with the plasticity test, it is an excellent criterion of abnormality and consequently of the need for varying manufacturing conditions to obtain optimum results, but it gives little information concerning the value of the rubber when made into commercial articles, and it may give misleading information concerning the behavior of the rubber in modern accelerator mixings.

An illustration of the first defect of using vulcanization in a rubber-sulfur mixing as the *sole* criterion of quality is found in tests carried out some time ago on samples of rubber containing traces of copper deliberately added in connection with special experiments. These samples gave excellent results on vulcanization, and it might have been concluded that the quality of the samples was not affected by the copper; nevertheless the vulcanized material perished quickly on keeping.

The second defect has been referred to by Dinsmore and Zimmerman (*Ind. Eng. Chem.*, **18**, 144 (1926)), who showed that uniformity in a rubber-sulfur mixing does not always correspond with uniformity in an accelerator mixing.

When evaluating raw rubber for general purposes, therefore, it is necessary to carry out at least two supplementary experiments in addition to plasticity tests and vulcanization in a rubber-sulfur mixing. These supplementary tests are discussed below and consist of (1) an aging test, (2) an accelerator-mixing vulcanization test.

Aging Tests.—To determine the value of rubber when made into manufactured articles, some form of aging test is essential.

The aging tests of the Ceylon Rubber Research Scheme are carried out in air at atmospheric pressure at 70° C., after vulcanization in a rubber sulfur mixing to a suitable condition. There is no doubt that the results of tests are at least in approximate accord with the results of natural aging, *e. g.*, a rubber containing

traces of copper soon perishes at 70° C., so does acetone-extracted rubber and rubber prepared by the acid coagulation of preserved latex, and all of these perish more quickly than usual when kept at ordinary temperatures.

This artificial test has been extremely useful in comparing the properties of air-dried and smoked sheet. The results vary with the condition of drying, but invariably the specially prepared samples of air-dried sheet have perished more quickly than smoked sheet.

	Time of Vulcani- zation, Hrs.	Tensile Strength (Lbs./ Sq. In.) after Aging, Hrs.				Elongation, Per Cent, at Load of 1.04 Kg./Sq. Mm. after Aging, Hrs.			
		Nil.	48	96	144	Nil	48	96	144
Smoked sheet.....	96	1820	2450	2080	1470	871	771	720	680
Air-dried sheet.....	82	1920	2320	300	220	865	743

It is not proposed to discuss the reason for the poor aging of air-dried sheet, as this paper is solely concerned with the evaluation of raw rubber. These results are given to emphasize the importance of the artificial aging test. It must not be concluded, however, that sheet, which has not been dried in smoke always has poor aging properties, as modifications of the method of preparation have a considerable influence on the results of tests.

Plasticity and vulcanization tests indicated that although air-dried sheet was different from smoked sheet the differences merely affected factory operations, and it was concluded that they were not of importance as long as the rubber was uniform. The artificial aging test, however, indicates that the rubber might be inferior when made into manufactured goods. This is more serious, though no doubt the addition of antioxidants would remove the inferiority even as it does when copper is present.

Accelerated Mixings.—The evaluation of rubber by vulcanization in an accelerator mixing is complicated by the fact that much depends upon the type of mixing selected. Investigation by the staff of the Ceylon Rubber Research Scheme indicates that there are two types of variation, one connected with the amount of fatty acid in the rubber and the other possibly with serum accessory substances.

In the absence of fatty acids, inorganic accelerators such as litharge are ineffective, and most organic accelerators require larger quantities of zinc oxide to produce full activation (Davey, *J. Soc. Chem. Ind.*, 49, 338T (1930)). Nearly all first grade rubber contains a little over 1 per cent of fatty acid, but inferior grades and rubber which has been stored for a long time may contain much less. It is very exceptional therefore to find first grade rubber causing any trouble, owing to the amount of fatty acids present. The use of inferior grades, however, may lead to considerable difficulty.

The second type of variation in accelerator mixings has not yet received the thorough investigation it deserves. It only occurs in those mixings in which the amount of sulfur and accelerator is reduced as low as possible. This is shown in the following table, which deals with results of tests on two samples of rubber in which the amount of sulfur and accelerator in the mixing was reduced from that employed by the Ceylon Rubber Research Scheme to that employed by Dinsmore and Zimmerman, who claim that rubber is variable in the presence of organic accelerators.

It is evident that a considerable amount of variation may occur when rubber is used in mixings in which the proportion of sulfur and of accelerator is low. As many manufacturers reduce the amount of sulfur as much as possible, it is evident that this type of variation is of considerable importance. It may be added that tests on 48 estate samples showed that there was little variation when the

mixing containing the largest amount of sulfur and accelerator was employed. Extensive tests have not yet been made with the mixing containing the smallest quantities of sulfur and accelerator. It is evident, however, that this is the type of accelerator mixing which should be selected for the general evaluation of raw rubber because it will not only reveal a deficiency of fatty acids in the rubber, but also the possibility of other variations when using the rubber in accelerator mixings.

Mixing per 100 Parts of Rubber			Time of Vulcanization at 148° C., Hrs.	Sample 1215		Sample 1225	
Zinc Oxide	Sulfur	Diphenylguanidine		Tensile Strength, Lbs./Sq. In.	Elongation at Load of 1.04 Kg./Sq. Mm., %	Tensile Strength, Lbs./Sq. In.	Elongation at Load of 1.04 Kg./Sq. Mm., %
5.6	5.6	1.1	25	2880	573	2990	580
6.0	5.5	0.4	20	1200	935	1750	877
			30	1550	870	1900	861
			40	1830	820	1980	759
			20	590	...	1250	1035
6.0	2.75	0.4	30	680	...	1790	931
			40	1010	935	1750	877

No investigation has yet been made of the effect of accelerators on air-dried sheet, but there is no doubt that this test is essential before attempting to market a new form of rubber on a large scale.

General Remarks.—A large variety of tests have been suggested at different times for the evaluation of raw rubber for general purposes. It is considered, however, that the tests should be as simple and practical as possible. They are therefore reduced to the minimum consistent with reliable evaluation. These tests indicate:

- (1) How the rubber is likely to behave in manufacturing operations.
- (2) General abnormality,
- (3) Dependability to age well,
- (4) Response to accelerators.

They consist of:

- (1) A mastication test,
- (2) A vulcanization test in a rubber-sulfur mixing,
- (3) An aging test in a rubber-sulfur mixing,
- (4) A vulcanization test in an accelerator mixing.

The most suitable conditions for carrying out each test are discussed, and the results are illustrated by references to tests on air-dried and smoked sheet.

Before concluding, it should be pointed out that the evaluation of raw rubber has not received the attention it deserves. Rubber is still bought and sold on appearance. This is simple and convenient, but does not encourage a planter to pay attention to the intrinsic properties of his product. Manufacturers are the only ones who are in a position to insist that the best rubber should have specified properties. It is believed that some of them do, and similarly some planters display great interest in the intrinsic properties of the rubber which they market, but the whole rubber industry would benefit if it were organized to encourage the production of rubber with uniform intrinsic properties. This is unlikely, however, unless manufacturers take the initiative not only in formulating their requirements, but also in purchasing rubber from estates which produce rubber of the required quality.

Observations on the Coagulation of Hevea Latex

R. G. Fullerton

Introduction

A great deal of attention has been given to a study of coagulation phenomena in rubber latex, but, until recently, investigations have been hampered by the absence of a satisfactory method for the accurate definition of the various stages in the coagulation process in terms of the hydrogen ion concentration of the medium. Among the first to draw attention to the importance of establishing satisfactory methods for the measurement of hydrogen ion concentration was Belgrave,¹ who made use of the hydrogen electrode and compared the results of electrometric measurements with those obtained colorimetrically by means of indicators. He found that results obtained electrometrically in this way were uncertain, owing to coagulation of the latex on the platinized hydrogen electrode, and with indicators it is difficult to make colorimetric comparisons when working with a cloudy liquid. More recently, however, van Harpen² and van Dillen³ have made use of the quinhydrone electrode to make more accurate observations of the various stages in the process. The present paper describes some observations which have been made with the aid of the quinhydrone electrode applied to the study of hydrogen ion concentration of latex under the influence of acids and certain preservatives.

Technic

The technic followed in the making of measurements and the assembly of the apparatus followed very closely that recommended by Biilmann and Tovborg-Jensen⁴ for the determination of p_H values in soil-water mixtures. In both electrodes the metallic electrode used was a piece of bright platinum foil, about 1 centimeter square, welded to a platinum wire fused into a glass tube. The standard electrode used was the quinhydrone electrode, the electrolyte of which was prepared by mixing 900 cc. of 0.1 *N* KCl, with 100 cc. of 0.1 *N* HCl. The potential was measured by means of the portable type of potentiometer supplied by the Cambridge Instrument Co., Ltd. Before making a series of determinations, the apparatus was standardized by measuring the p_H in a standard buffer solution of known composition. For this purpose an 0.05 *M* solution of potassium hydrogen phthalate was used, the p_H of which is 3.97 between 20° and 30° C. The quinhydrone was prepared according to the methods recommended by Biilmann and Lund,⁴ 0.1 g. of the solid being added per 25 cc. of solution in either of the two electrode vessels.

For this system Biilmann has developed the equation:

$$p_H = 2.03 + \frac{\pi}{0.0001984 \times T}$$

where π is the measured potential in volts and T is the absolute temperature. He has shown that for a temperature fluctuation in the electrode of $\pm 1^\circ \text{C.}$, the error introduced is not greater than 0.05 of a unit of p_H . Since room temperature in the tropics is fairly constant at $29 \pm 1^\circ \text{C.}$, a thermostat was not used in the

experiments to be described. For each single measurement the temperature of the solution, whose p_H was to be determined, was recorded, and it was found that the average fluctuation about the value 29°C. was 0.5° .

For determinations of the p_H of latex in a state of flocculation or coagulation, the p_H values of the sera were obtained.

Before proceeding with the main investigation, it was necessary to determine: (a) whether there is an appreciable drift of potential in making a measurement with latex, and (b) the accuracy with which results can be reproduced for the same latex within reasonable limits of time.

To determine the first point, fresh undiluted latex and the same latex diluted to a low rubber content were examined. Two samples—A and B—from different groups of trees on the same estate were collected shortly after tapping. Diluted latices, in the proportion: latex : water = 1:9, were prepared from each of the two original samples, and all four latices allowed to stand for about 15 minutes with occasional gentle stirring. Measurements were then taken in the order—sample A undiluted, sample A diluted, sample B undiluted, sample B diluted. For each series of measurements the procedure was as follows:

Quinhydrone was added to a portion of the sample in a test tube—about 0.1 g. per 25 cc. latex—and the mixture stirred together for a few seconds with a glass rod. The test tube with contents was then placed in position in the apparatus which had previously been standardized and tested. A reading for e. m. f. was then taken as soon as possible, and the time for this referred to as zero. Read-

TABLE I
DRIFT OF POTENTIAL WITH TIME

Latex Sample A				Latex Sample B			
Undiluted		Diluted 1:9		Undiluted		Diluted 1:9	
Time in Secs.	p_H	Time in Secs.	p_H	Time in Secs.	p_H	Time in Secs.	p_H
0	6.80	0	6.48	0	6.81	0	6.42
10	6.80	10	6.48	10	6.81	10	6.42
20	6.80	20	6.48	20	6.81	20	6.42
30	6.80	30	6.48	30	6.81	30	6.42
40	6.80	40	6.48	40	6.81	40	6.42
50	6.79	50	6.48	50	6.80	50	6.42
60	6.79	60	6.47	60	6.80	60	6.41
70	6.79	70	6.47	70	6.80	70	6.41
80	6.79	80	6.47	80	6.80	80	6.41
90	6.79	90	6.47	90	6.80	90	6.41
100	6.79	100	6.47	100	6.80	100	6.41
130	6.79	110	6.47	110	6.80	110	6.41
160	6.79	120	6.47	120	6.80	120	6.41
190	6.79	120	6.47	130	6.80	130	6.41
220	6.78	140	6.47	140	6.80	140	6.41
250	6.78	150	6.47	150	6.80	150	6.41
280	6.78	160	6.46	160	6.80	160	6.40
310	6.77	170	6.46	170	6.80	170	6.40
340	6.77	200	6.46	180	6.79	200	6.40
370	6.77	230	6.46	190	6.79	230	6.39
400	6.76	290	6.45	200	6.79	290	6.39
430	6.76	350	6.45	230	6.79	350	6.39
460	6.76	370	6.45	260	6.79	370	6.39
490	6.74	390	6.45	290	6.77	390	6.37
520	6.74	410	6.43	310	6.77	400	6.37
550	6.74	430	6.43	340	6.77	430	6.37
580	6.73	450	6.43	370	6.77	450	6.36
610	6.73	470	6.42	400	6.76	470	6.36
After 4 hours	6.50	After 4 hours	6.24	After 4 hours	6.55	After 4 hours	6.22

ings were than taken for the sample at definite intervals, usually 10 seconds, over a total period of about 10 minutes. The test tube was then removed, and the platinum electrode was cleaned by rinsing with distilled water and heating to redness. The apparatus was then standardized and made ready for the next series of measurements. The p_H of all four samples was then determined after a period of four hours. Table I summarizes the results obtained. It will be seen that the potential attains its maximum value almost immediately, and there is, thereafter, a slight drift in the direction of decreasing p_H . In what follows, therefore, the initial reading for the e. m. f. was taken as the true value.

As regards agreement in repeat measurements, Table II gives the results of a few determinations for two samples of fresh latex—A and B—and latices prepared from each of these by dilution with distilled water, as before in the proportion latex:water = 1:9. The procedure was to stir the bulked latex thoroughly and then pour about 15 cc. into each of a series of glass tubes of approximately the same diameter in order that uniform conditions might obtain. Measurements were then carried out at definite intervals of time for each member of this series of samples. It will be seen that the values for latex, both diluted and undiluted remain fairly constant within a period of about one-half hour, which period is of course ample in practice for the performance of several determinations of p_H .

TABLE II
AGREEMENT IN READINGS FOR A SERIES OF SAMPLES TAKEN FROM THE SAME LATEX

Latex Sample A				Latex Sample B			
Undiluted		Diluted 1:9		Undiluted		Diluted 1:9	
Time, Mins.	p_H	Time, Mins.	p_H	Time, Mins.	p_H	Time, Mins.	p_H
0	6.80	0	6.52	0	7.01	0	6.77
5	6.81	12	6.52	5	7.00	10	6.77
10	6.79	27	6.51	10	7.01	21	6.75
15	6.80	37	6.52	15	7.00	30	6.76
20	6.80	47	6.54	20	7.01	35	6.77
25	6.80	66	6.52	25	7.02	45	6.77
30	6.81	77	6.54	30	7.00	65	6.76
35	6.79	85	6.53	35	7.01	80	6.75

In what follows, before each determination of p_H it was found necessary to rinse the negative electrode with distilled water and to heat the platinum to redness in a sulfur-free flame.

EXPERIMENTAL

A. Fresh Latex

If latex is examined within about 2 hours after its exudation from the tree, it is found to be very nearly neutral. The p_H values of a large number of samples collected at various periods of the year ranged from 7.02 to 6.80. If the latex is allowed to stand so that its surface is exposed to the atmosphere, for the first 5 or 6 hours after tapping, the p_H remains very nearly constant. Thereafter clotting commences, accompanied by a more rapid increase in hydrogen ion concentration, until finally within a period of about 24 hours coagulation takes place. The coagulation is not, however, usually complete, that is to say, one does not find only a coherent coagulum floating in a clear serum. If the storage vessel is of sufficient depth, one finds on the surface a shallow layer of thick alkaline slime of fairly high rubber content, then a deeper layer of coherent coagulum, and beneath a watery serum with a distinctly acid reaction, usually milky and still containing a few latex particles in suspension. In Table I the figures for undiluted latex show the course of the changes in hydrogen ion concentration within the first 4 hours after tapping. It is not possible to measure with a great degree of

accuracy by the quinhydrone electrode the p_H of the various layers which form as the result of this spontaneous coagulation, since the changes are accompanied by a free evolution of hydrogen sulfide gas, which may bring about poisoning of the electrodes. By means of indicators, however, it was ascertained that the p_H of the surface layer was, in the cases examined, distinctly on the alkaline side of neutrality—from 7.5 to 8.0—while the p_H of the serum resulting from the coagulation ranged from 6.3 to 6.5.

If a series of latex samples is prepared and examined in order of increasing hydrogen ion concentration, it is found that there is first a range of p_H values defining a condition of the sol which may be described as complete dispersion. By this is meant that no aggregation of the latex particles sufficient to cause separation of the whole or part of the disperse phase has taken place. This is followed by a range or zone within which the latex is coagulated. For still higher values of hydrogen ion concentration, there is again a zone of complete dispersion, and finally at the end of the scale a further range within which coagulation is again complete. As will be shown later, the degree of dispersion in the various zones is influenced by several factors, principally by the rubber content of the latex, the transition from one zone or range to another is gradual, and, depending on the dilution of the latex, another set of values defining a condition intermediate between coagulation and dispersion may be obtained. Such a discontinuity has been observed in the flocculation of other colloidal sols by electrolytes—*e. g.*, the flocculation of a negatively charged sol of mastic by $AlCl_3$ —and these phenomena have been designated by the term "irregular series."

In studying the different zones defining various conditions of the dispersion, the procedure was to add increasing quantities of an acid coagulant in fixed concentration to a series of latex samples of equal volume, and to examine the samples after a period of 24 hours. By choosing coagulation vessels of the same shape and dimensions for each member of the series, conditions under which changes in the p_H of the system might occur within the period allowed for examination were kept as uniform as possible. Within such a period, sufficient time is allowed for changes that occur in the dispersion to reach a stage at which they can be definitely characterized by their appearance and other properties. For example, the initial stages in coagulation may occur four hours after the addition of the coagulant without the visible separation of the latex into two layers, coagulum and serum. It is therefore difficult to characterize the condition of the dispersion at this stage. After a further period, however, the process may have reached a stage at which separation into coagulum and serum is distinctly discernible, and where from the appearance of the serum the coagulation may be described as partial or complete, as the case may be. By the addition of the coagulant in the manner stated, the initial dry rubber content of the latex is lowered, but the concentration of the coagulant was so chosen that the dilution of the latex caused by its addition was very slight. When a greater interpolation of p_H values was required for the transition from one boundary to another, a suitable buffer salt solution was added to the latex before the addition of the coagulant.

In tabulating the results the following system is adopted for the description of the condition of the dispersion after the period stated.

Complete Dispersion.—This describes a condition where the latex is homogeneous and completely liquid, having the same appearance microscopically as pure latex examined soon after tapping. The particles are in vigorous Brownian motion and aggregation of the particles has not occurred to such an extent that there is a separation of rubber from the dispersion, either in the form of a flocculate or a coherent clot of coagulum.

Partial Flocculation.—There is a separation from the dispersion of floccules which can be seen microscopically to consist of large aggregates of smaller rubber particles. The separation to the surface in the form of a flocculate is not complete, the underlying serum being milky in appearance and still containing a high proportion of rubber particles in suspension. The flocculate can be re-dispersed by shaking the tube and separation does not thereafter recommence for a considerable time.

Complete Flocculation.—The separation of rubber from the latex in the form of a flocculate is complete, the underlying serum being water-clear and practically free from rubber globules in suspension. As in the case of partial flocculation, the same remarks apply to the reversibility of the flocculate.

Partial Coagulation.—There is a separation in the form of a coherent coagulum or clot, but a large proportion of rubber remains in suspension in the serum, which is milky white in appearance.

Coagulant Almost Complete.—There is a separation in the form of a coherent irreversible coagulum, but the separation is not complete. The underlying serum is slightly cloudy, and still contains a small proportion of rubber particles in suspension.

Complete Coagulation.—There is complete separation in the form of a coherent coagulum and a clear serum.

In Diagram I an attempt has been made to present the salient features differentiating the various conditions described above. The diagram has been constructed from the data set forth for the third series in Table III, which will be discussed later.

Latex of 4 Per Cent Rubber Content

By working with latex of low rubber content, it is possible to demonstrate more clearly than with undiluted latex the gradual changes which accompany the transition from one zone to another. Fresh latex was diluted to a dry rubber content of 4 per cent and buffered with a 10 per cent solution of ammonium acetate before the addition of the coagulant in the form of a 2.5 per cent solution of acetic acid.

The buffer solution was added in three different proportions, and corresponding to each proportion a separate series of latex samples was prepared. Table III summarizes the results obtained. In the first series complete coagulation occurs at a p_H of 4.81, in the second at p_H of 4.84, and in the third at p_H of 4.83. It will be seen that the transition from a condition of complete dispersion, or from the first liquid zone to the first coagulation zone, is accompanied by a progressive series of changes. With increasing hydrogen ion concentration, we pass through intermediate stages of partial coagulation before complete coagulation results. The third series gives the clearest picture of what occurs since here the gradations in p_H are smaller. By reference to Table III and to Diagram I, it will be seen that the transitional stage is defined by the range p_H 5.30 to 4.91.

On repeating this experiment with latex collected from the same group of trees on different days, different results were obtained for the p_H values defining the commencement of complete flocculation and of complete coagulation. Table IV shows how these values vary. The transition is irregular and somewhat ill defined. Taking the average of the values obtained, one finds that complete flocculation commences at p_H 5.03 and complete coagulation at p_H 4.87. Van Harpen,² working in Sumatra, finds for latex of approximately the same rubber content the values p_H 5.05 and p_H 4.77, respectively. It is probable that differences in latex composition are responsible.

In order to bring the latex into the second liquid zone or second zone of complete dispersion, a stronger acid is required as coagulant.

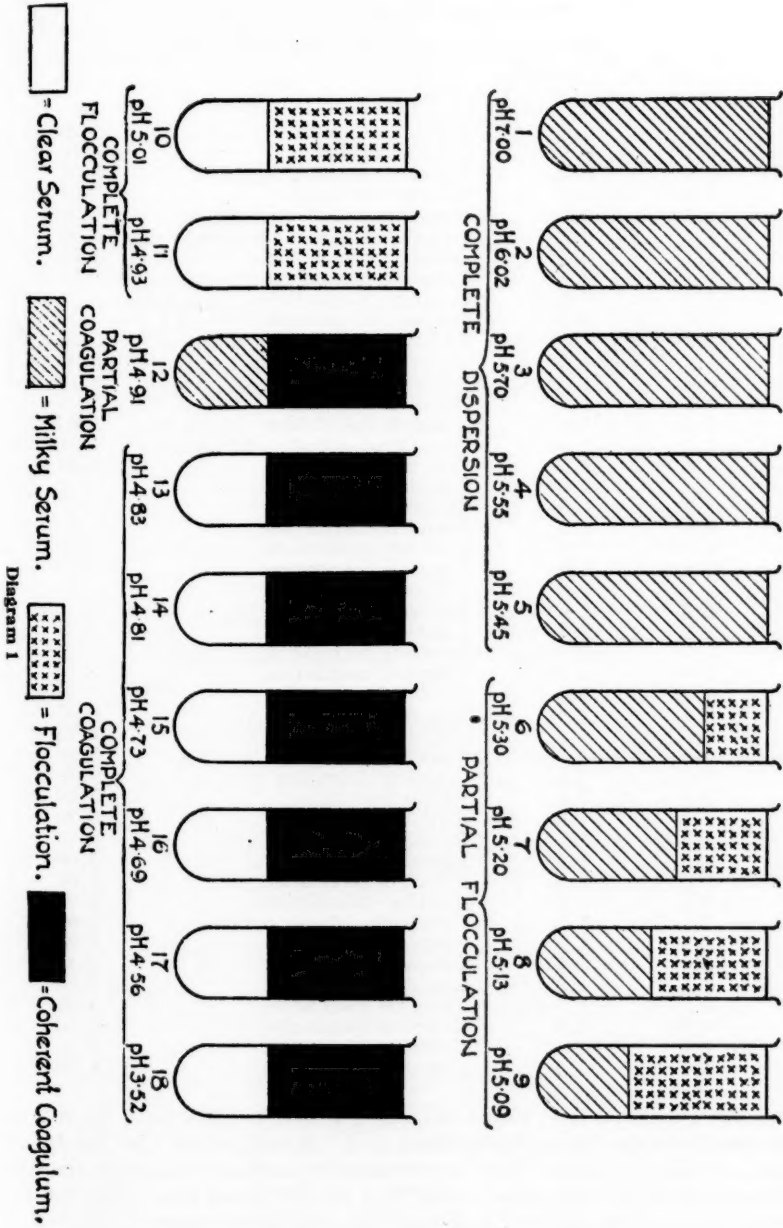


TABLE III
FRESH LATEX

Dry Rubber Content = 4 Per Cent
First Liquid Zone to First Coagulation Zone

Cc. of 2.5 Per Cent Acetic Acid per 50 Cc. Latex	Cc. of 10 Per Cent Ammonium Acetate per 50 Cc. Latex	Condition after 24 Hours	p _H
0.2	0.5	Partial flocculation	5.29
0.4	0.5	Partial flocculation	5.16
0.6	0.5	Partial flocculation	5.03
0.8	0.5	Partial flocculation	5.01
1.0	0.5	Coagulation almost complete	4.98
1.2	0.5	Coagulation almost complete	4.89
1.4	0.5	Complete coagulation	4.81
1.6	0.5	Complete coagulation	..
1.8	0.5	Complete coagulation	..
2.0	0.5	Complete coagulation	..
0.2	1.0	Partial flocculation	5.32
0.4	1.0	Partial flocculation	5.20
0.6	1.0	Partial flocculation	5.13
0.8	1.0	Complete flocculation	5.08
1.0	1.0	Complete flocculation	4.96
1.2	1.0	Coagulation almost complete	4.91
1.4	1.0	Complete coagulation	4.84
1.6	1.0	Complete coagulation	..
1.8	1.0	Complete coagulation	..
2.0	1.0	Complete coagulation	..
2.2	1.0	Complete coagulation	..
2.4	1.0	Complete coagulation	..
2.6	1.0	Complete coagulation	..
2.8	1.0	Complete coagulation	..
3.0	1.0	Complete coagulation	..
3.2	1.0	Complete coagulation	..
3.8	1.0	Complete coagulation	..
4.0	1.0	Complete coagulation	..
0.2	1.5	Complete dispersion	6.02
0.6	1.5	Complete dispersion	5.70
0.8	1.5	Complete dispersion	5.55
0.9	1.5	Complete dispersion	5.45
1.0	1.5	Partial flocculation	5.30
1.3	1.5	Partial flocculation	5.20
1.5	1.5	Partial flocculation	5.13
1.8	1.5	Partial flocculation	5.09
2.0	1.5	Complete flocculation	5.01
2.2	1.5	Complete flocculation	4.93
2.5	1.5	Coagulation almost complete	4.91
2.8	1.5	Complete coagulation	4.83
3.0	1.5	Complete coagulation	4.81
3.5	1.5	Complete coagulation	4.73
3.7	1.5	Complete coagulation	4.69
4.0	1.5	Complete coagulation	4.66
4.5	1.5	Complete coagulation	4.63
4.7	1.5	Complete coagulation	4.56

This also applies for latex within the second zone of coagulation. Table V shows the results obtained using hydrochloric acid. It will be seen that the transition from one zone to another is not accompanied by so many changes in the state of dispersion as is the case when passing from the first liquid zone to the first coagulation zone, and the ranges of p_H defining the transitional stages are smaller. The flocculated condition does not make its appearance, though the gradations in p_H are small. Taking the series in order of increasing hydrogen ion concentra-

tion, in the passage from the first coagulation zone to the second liquid zone a condition of complete dispersion first makes its appearance at p_H 3.52, and this condition persists until a p_H of 0.83 is reached, until complete coagulation results at a p_H value of 0.82.

The foregoing results are conveniently summarized in Table VI.

TABLE IV
FRESH LATEX
Dry Rubber Content = 4 Per Cent

Date of Tapping	p_H , Complete Flocculation	p_H , Complete Coagulation
22-6-29	5.01	4.74
23-6-29	5.08	4.78
24-6-29	4.98	4.93
25-6-29	5.11	4.96
1-7-29	5.00	4.87
3-7-29	4.95	4.84
4-7-29	5.03	4.74
5-7-29	5.02	4.88
15-7-29	4.96	4.88
18-7-29	5.02	4.87
19-7-29	5.14	5.04
Average	5.03	4.87

TABLE V
FRESH LATEX
Dry Rubber Content = 4 Per Cent
First Coagulation Zone to Second Liquid Zone

Cc. 0.1 N HCl per 50 Cc. Latex	Condition after 24 Hours	p_H
0.5	Incomplete flocculation	..
1.0	Incomplete flocculation	..
1.5	Complete coagulation	4.74
2.0	Complete coagulation	..
2.5	Complete coagulation	3.80
2.6	Coagulation almost complete	3.71
2.7	Coagulation almost complete	3.65
2.9	Coagulation almost complete	3.58
3.0	Complete dispersion	3.52
3.5	Complete dispersion	3.20

Second Liquid Zone to Second Coagulation Zone

Cc. of N HCl per 50 Cc. Latex	Condition after 24 Hours	p_H
0.8	Complete dispersion	2.01
4.8	Complete dispersion	1.26
6.0	Complete dispersion	1.00
7.0	Partial coagulation	0.88
8.0	Partial coagulation	0.87
9.0	Partial coagulation	0.83
10.0	Complete coagulation	0.82
11.0	Complete coagulation	0.76
12.0	Complete coagulation	0.74
13.0	Complete coagulation	0.71
14.0	Complete coagulation	0.67
15.0	Complete coagulation	0.66
16.0	Complete coagulation	0.62

TABLE VI
FRESH LATEX
Dry Rubber Content = 4 Per cent

	p_H Range
Complete dispersion.....	>5.30
Partial flocculation.....	5.30-5.01
Complete flocculation.....	5.01-4.91
Coagulation almost complete.....	4.91-4.83
Complete coagulation.....	4.83-3.80
Coagulation almost complete.....	3.80-3.52
Complete dispersion.....	3.52-1.00
Partial coagulation.....	1.00-0.82
Complete coagulation.....	<0.82

Latex of 15 Per Cent Rubber Content

Dilution of the latex to a rubber content of 15 per cent which is the standard dilution usually adopted in Malayan plantation practice, does not create very marked differences compared with latex of greater dilution in the ranges of p_H values defining the various zones in the irregular series. As will be seen from Tables VII and VIII and Table IX, which summarizes the results, there is a more extended range of values within which complete coagulation takes place in the first zone, and the range for flocculation is smaller. The first appearance of a flocculate occurs at p_H 5.54, whereas in the previous case the lower value of 5.30 is required to bring about the first evidence of coagulation.

TABLE VII
FRESH LATEX
Dry Rubber Content = 15 Per Cent
First Liquid Zone to First Coagulation Zone

Cc. of 2.5 Per Cent Acetic Acid per 50 Cc. of Latex	Cc. of 10 Per Cent Ammonium Acetate per 50 Cc. of Latex	Condition after 24 Hours	p_H
0	1.0	Complete dispersion	6.96
0.2	1.0	Complete dispersion	6.20
0.6	1.0	Complete dispersion	5.82
1.0	1.0	Partial flocculation	5.54
1.2	1.0	Partial flocculation	..
1.4	1.0	Partial flocculation	..
1.8	1.0	Coagulation almost complete	5.24
2.0	1.0	Coagulation almost complete	..
2.2	1.0	Coagulation almost complete	..
2.4	1.0	Coagulation almost complete	5.04
2.6	1.0	Coagulation almost complete	4.94
3.0	1.0	Coagulation almost complete	4.82
3.5	1.0	Complete coagulation	4.78
3.8	1.0	Complete coagulation	..
4.0	1.0	Complete coagulation	..

First Coagulation Zone to Second Liquid Zone

Cc. of N HCl per 50 Cc. of Latex	Condition after 24 Hours	p_H
0.2	Complete dispersion	..
0.4	Coagulation almost complete	..
0.6	Complete coagulation	..
0.8	Complete coagulation	..
1.0	Complete coagulation	3.70
1.2	Complete coagulation	3.51
1.3	Coagulation almost complete	3.24
1.4	Coagulation almost complete	3.01
1.5	Complete dispersion	3.00
2.0	Complete dispersion	..
3.0	Complete dispersion	..

TABLE VIII
FRESH LATEX

Dry Rubber Content = 15 Per Cent

Cc. of 10 N HCl per 50 Cc. of Latex	Condition after 24 Hours	p_H
0.2	Complete dispersion	1.62
0.4	Complete dispersion	..
0.6	Partial coagulation	1.23
0.8	Partial coagulation	..
1.0	Partial coagulation	0.95
1.5	Complete coagulation	0.74

TABLE IX
FRESH LATEX

Dry Rubber Content = 15 Per Cent

	p_H Range
Complete dispersion.....	>5.54
Partial flocculation.....	5.54-5.24
Coagulation almost complete.....	5.24-4.78
Complete coagulation.....	4.78-3.51
Coagulation almost complete.....	3.51-3.01
Complete dispersion.....	3.01-1.23
Partial coagulation.....	1.23-0.73
Complete coagulation.....	>0.73

Latex of 20 Per Cent Rubber Content

For the sake of brevity the detailed experimental results are not reproduced for latex diluted to a rubber content of 20 per cent, and Table X gives a summary. From this it will be seen that there is now a marked difference in the progress of the series. In the first place coagulation makes its appearance at a higher value than in the two preceding cases, *viz.*, at p_H 5.80. But the main difference is found in the range of values within which latices of greater dilution are in the condition defined by the second liquid zone. With latex of 20 per cent dry rubber content, between p_H 3.02 and 0.60, a small clot of coherent coagulum is formed, though the rest of the latex remains in a state of complete dispersion. The percentage of the total rubber content separating as a clot was found to be roughly 2 per cent, the rest remaining in stable dispersion in the serum. There is, therefore, strictly speaking, no second liquid zone with latex of this rubber content. It will be seen also that a slightly higher hydrogen ion concentration is required before complete coagulation appears in the second coagulation zone—*viz.*, p_H 0.60—and that a region of flocculation does appear.

TABLE X
FRESH LATEX

Dry Rubber Content = 20 Per Cent

	p_H Range
Complete dispersion.....	>5.80
Coagulation almost complete.....	5.80-4.84
Complete coagulation.....	4.84-3.51
Coagulation almost complete.....	3.51-3.02
Partial coagulation.....	3.02-0.60
Complete coagulation.....	<0.60

Latex of Rubber Content = 35 Per Cent

Undiluted field latex was used for the tests, and the differences here are very marked. The detailed results of a typical experiment are set out in Table XI,

and summarized in Table XII. Here coagulation first appears at a still higher value than in previous cases—*viz.*, p_H 6.24—and flocculation does not occur. There is no second liquid zone. Within the range defined by p_H 3.02 to 0.83, coagulation is almost complete, and the serum is slightly milky. There are, therefore, only two zones in the series—a liquid zone and a coagulation zone.

TABLE XI

FRESH LATEX

Dry Rubber Content = 35 Per Cent

Cc. of 2.5 Per Cent Acetic Acid per 50 Cc. of Latex	Cc. of 10 Per Cent Ammonium Acetate per 50 Cc. of Latex	Condition after 24 Hours	p_H
0.5	0.5	Complete dispersion	6.31
1.0	0.5	Partial coagulation	6.20
2.0	0.5	Partial coagulation	..
3.0	0.5	Partial coagulation	..
4.0	0.5	Partial coagulation	..
5.0	0.5	Complete coagulation	4.71
7.0	0.5	Complete coagulation	..
Cc. of <i>N</i> HCl per 50 Cc. of Latex			
0.05	Nil	Complete dispersion	6.28
0.2	Nil	Partial coagulation	6.24
0.3	Nil	Partial coagulation	..
0.4	Nil	Partial coagulation	..
0.5	Nil	Partial coagulation	5.31
1.0	Nil	Complete coagulation	4.49
2.0	Nil	Complete coagulation	3.37
2.2	Nil	Coagulation almost complete	3.02
2.4	Nil	Coagulation almost complete	2.78
2.5	Nil	Coagulation almost complete	2.65
3.2	Nil	Coagulation almost complete	2.11
3.4	Nil	Coagulation almost complete	..
3.6	Nil	Coagulation almost complete	1.91
3.8	Nil	Coagulation almost complete	..
4.0	Nil	Coagulation almost complete	1.53
4.5	Nil	Coagulation almost complete	..
5.0	Nil	Coagulation almost complete	1.28
5.5	Nil	Coagulation almost complete	..
6.0	Nil	Coagulation almost complete	1.16
Cc. of 10 <i>N</i> HCl Per 50 Cc. of Latex			
1.0	Nil	Coagulation almost complete	..
1.5	Nil	Complete coagulation	0.83
2.0	Nil	Complete coagulation	..

TABLE XII

FRESH LATEX

Dry Rubber Content = 35 Per Cent

	p_H Range
Complete dispersion.....	>6.24
Partial coagulation.....	6.24-4.71
Complete coagulation.....	4.71-3.02
Coagulation almost complete.....	3.02-0.83
Complete coagulation.....	<0.83

B. Heated Latex

A study of the progress of changes in latex which has been boiled or pasteurized shows certain deviations from the normal course of the irregular series for pure field latex. Preparation was carried out according to the method which de Vries and Beumée-Nieuwland⁶ adopt for boiled latex or "B" liquid. This was carried out by boiling nine volumes of water and quickly pouring in one volume of latex, boiling the mixture for a further period of three minutes and then allowing to stand for five minutes before cooling in running water to the temperature of the room. Latex so prepared remains as a fairly stable dispersion for several days. Experimental work with this latex was carried out on the day of preparation, and the definitions adopted for the various states of dispersion are the same as those described for fresh latex.

To a portion of this "B" liquid, a solution of sodium oleate was added, so that the concentration of soap in the latex was 0.01 per cent by volume.

A sample of pure field latex diluted to the same rubber content, *viz.*, 4 per cent, was treated similarly.

A comparison was then made between the three samples: (1) "B" liquid, (2) "B" liquid + 0.01 per cent of sodium oleate, (3) fresh latex + 0.01 per cent of sodium oleate. The experimental results are summarized in Table XIII.

The observations of other workers, notably de Vries⁶ and Belgrave,⁷ are confirmed to the effect that "B" liquid merely flocculates for values of p_H for which fresh latex coagulates within the first coagulation zone. Coagulation does not occur until a p_H of 0.80 is reached, a value which is practically the same as that observed for pure field latex. For "B" liquid the definitive values of p_H for the various zones agree closely with those obtained by van Harpen.²

By the addition of a small quantity of sodium oleate to "B" liquid, however, coagulation takes the same course as for pure latex—between p_H 4.68 and 3.50 complete coagulation is obtained. In other words the addition of sodium oleate has brought about a coalescence of the floccules.

As compared with pure field latex of the same dilution, it will be seen from Table XIII Column (3) that the addition of sodium oleate has caused the first appearance of separation from the dispersion to commence at a slightly lower hydrogen ion concentration, *viz.*, p_H 5.24. Also coagulation is first complete at p_H 4.95, compared with the value 4.83 for pure latex.

During the course of this work, it was noted that there is on occasions a slight rise in p_H on heating. Samples were prepared from the same stock of fresh latex in the same way as for "B" liquid, except that the temperature of heating was varied from room temperature (29° C.) to 100° C. The measurements of p_H were carried out when all the samples of the series had cooled to room temperature. Other conditions during preparation were kept as uniform as possible for each member of the series. Table XIV, which gives the results obtained for two series prepared from different stock latices, A and B, shows that the p_H tends to increase as the temperature of heating increases. The two cases quoted are, however, extreme. With some samples the rise in p_H was very slight, though in all cases it was appreciable. A possible explanation is that carbon dioxide is lost from the system on heating, thereby decreasing the acidity. Another factor which possibly acts in conjunction with the loss of carbon dioxide is the rise of p_H , which may take place as a result of denaturation of the proteins, since almost certainly some of the proteins are denatured by heating the latex to a high temperature. A rise of p_H taking place as the result of the heat denaturation of egg albumin solutions has been observed by Chick and Martin.⁸

TABLE XIII

Condition	(1) "B" Liquid	Ranges of p_H	
		(2) "B" Liquid +0.01 Per Cent of Sodium Oleate	(3) Fresh Latex +0.01 Per Cent of Sodium Oleate
Dispersion.....	>5.02	>5.01	>5.24
Flocculation.....	5.02-3.52	5.01-4.68	5.24-4.95
Coagulation.....	Does not occur	4.68-3.50	4.95-3.51
Dispersion.....	3.52-0.80	3.50-0.82	3.51-0.83
Coagulation.....	<0.80	<0.82	<0.83

TABLE XIV

Latex A		Latex B	
Temperature of Heating, ° C.	p_H at 28° C.	Temperature of Heating, ° C.	p_H at 28° C.
28	6.68	28	5.92
35	6.70	35	5.93
40	6.73	40	5.94
45	6.77	43	5.99
51	6.82	50	6.41
55	6.91	55	6.52
60	6.91	62	6.61
65	6.86	65	6.61
70	6.90	70	6.62
76	6.91	75	6.62
80	6.99	80	6.62
90	6.99	90	6.62
100	7.19	100	6.64

C. Preserved Latex

The normal course of the irregular series observed for fresh field latex is markedly altered by the addition of certain preservative substances. The preservative most widely used in plantation practice is ammonia, but other substances are occasionally employed, chief among which are sodium hydroxide and formalin. The various preserved latices were diluted to a rubber content of 4 per cent, since at this dilution comparison of the effect of each preservative substance on coagulation is easily made, and, as with fresh field latex, the transitional stages between the various zones are easily defined. The acid coagulants used were the same for all samples examined.

(a) *Ammonia*.—The samples were prepared by the addition of a solution of ammonia of 0.891 specific gravity to fresh field latex, the concentrations of NH_3 in the various samples ranging from 0.30 to 0.80 per cent by weight, at the time of preparation. The samples were examined a few days after preparation and at intervals of about one month during a period of storage of ten months. It was found that differences in the period of storage and the quantity of ammonia added did not affect the ranges of hydrogen ion concentration defining the various states of dispersion in the coagulation series. For the sake of brevity the detailed experimental results are not reproduced, and the results are summarized in Table XV. Column (1) gives results which are typical of those obtained with all the samples of ammoniated latex. It will be seen that the results are almost the same as those obtained for pure field latex of the same dilution. This applies also to ammoniated latex of higher rubber content, though with undiluted latex there is a difference in behavior after the addition of the coagulant. With undiluted ammoniated latex coagulation is obtained almost immediately after the addition of the acid. The first few drops of acid produce local clotting, even

when the latex is thoroughly stirred during the addition, and with increasing quantities this clot increases in size until coagulation is complete. With pure latex, however, no such local clotting is observed, and several hours must elapse before coagulation is obtained. It may be stated therefore that ammoniated latex is more sensitive than pure latex to acid coagulants.

(b) *Sodium Hydroxide*.—The sample examined was prepared by adding a concentrated solution of sodium hydroxide to field latex to give a latex containing 0.8 per cent by weight of sodium hydroxide. The interesting feature is that the course of coagulation is affected by the length of the period of storage. When examined within two or three days after the addition of the preservative, it was found that coagulation did not take place for any value of p_H below 7.0 within a period of 24 hours after the addition of the coagulant. In other words, within this specified period the latex does not coagulate, whatever its hydrogen ion concentration. As will be seen from Table XV Column (2), which gives the results obtained on examination of the sample 2 days after the addition of the preservative, the latex merely flocculates for values of p_H at which fresh field latex coagulates, both in the first and in the second coagulation zones. There are two zones of flocculation in place of two zones of coagulation, separated by zones of complete dispersion. Latex within these flocculation zones remains in that state for several days without any evidence of coherent clot formation, but later the floccules gradually cohere and coagulation ensues. This applies also to sodium hydroxide latex of high rubber content. After the addition of the coagulant a coherent coagulum can be obtained only by mechanical kneading of the flocculated mass.

TABLE XV
PRESERVED LATEX

Dry Rubber Content = 4 Per Cent			
Ammonia	Sodium Hydroxide, Fresh	Sodium Hydroxide, Long Storage	Formalin
Complete dispersion >5.30	Complete dispersion >5.69	Complete dispersion >8.00 (Approx.)	Complete dispersion >4.56
Partial flocculation 5.30-5.01	Partial flocculation 5.69-4.78	Partial coagulation 8.00-4.76	Partial flocculation 4.56-4.36
Complete flocculation 5.01-4.92	Complete flocculation 4.78-3.39	Complete coagulation 4.76-3.01	Complete flocculation 4.36-3.41
Coagulation almost complete 4.92-4.81	Partial flocculation 3.39-3.00	Partial coagulation 3.01-1.03	Partial flocculation 3.41-3.27
Complete coagulation 4.81-3.79	Complete dispersion 3.00-1.01	Coagulation almost complete 1.03-0.63	Complete dispersion 3.27-1.07
Coagulation almost complete 3.79-3.51	Partial flocculation 1.01-0.63	Complete coagulation <0.63	Partial flocculation 1.07-0.66
Complete dispersion 3.51-1.02	Complete flocculation <0.63		Complete flocculation <0.66
Partial coagulation 1.02-0.82			
Complete coagulation <0.82			

When the same sample of latex treated with sodium hydroxide was examined after a longer period of storage, it was found that two zones of complete coagulation were obtained as for fresh field latex. Column (3) gives the results for a period of six months' storage. These are typical of those obtained when the latex was examined at intervals of one month after preparation. It is only when freshly prepared that such latex shows abnormal coagulation. Although normal coagulation is restored after longer storage, the latex is very sensitive to acid coagulants,

for local clotting takes place immediately after the addition of the acid even when the latex is dilute and at low values of p_H . It is thus still more sensitive than ammoniated latex. As will be seen from the table, clotting or partial coagulation commences at a p_H well on the alkaline side of neutrality, *viz.*, 8.00, though this value is approximate and had to be obtained colorimetrically by means of indicators, the quinhydrone electrode being inapplicable to solutions with a p_H greater than 8.0.

It will also be seen that there is no second liquid zone. Between the range p_H 3.01 and 1.03, which defines a state of complete dispersion in the case of pure latex, sodium hydroxide latex partially coagulates, approximately 50 per cent of the total rubber separating from the dispersion in the form of a coherent clot.

(c) *Formalin*.—Latex preserved by the addition of formalin behaves in much the same way as fresh latex treated with sodium hydroxide. The sample under discussion was prepared by the addition of a solution of formalin to give a concentration of formaldehyde in the latex of 0.4 per cent by volume, and the results given in column (4) of Table XV refer to the examination of the sample after a period of four months' storage. As with freshly prepared latex sodium hydroxide, coagulation does not occur within a period of 24 hours when the latex is diluted to a rubber content of 4 per cent whatever the period of storage. Comparing the ranges of p_H in column (4) with those in column (2), it will be seen that there are in both cases two zones of flocculation separated by two zones of complete dispersion, though in the case of latex treated with formalin the first appearance of the flocculation stage is associated with a higher hydrogen ion concentration— p_H 4.56 for formalin and 5.69 for sodium hydroxide. Otherwise the behavior of these two preserved latices is very similar.

(d) *Centrifuged Latex*.—When latex is subjected to centrifugal action, for example in a centrifuge of the De Laval type, separation into two latex fractions takes place. Owing to the difference in the specific gravities of the rubber particles and the dispersion medium, when the bowl of the centrifuge is rotated at a sufficiently high speed the rubber particles, being lighter, pass to the central axis of the bowl, while the serum flows toward the outside walls. The separation is, however, not complete. The cream fraction has a high rubber content, and

TABLE XVI
CENTRIFUGED LATEX
Dry Rubber Content = 4 Per Cent

Cream Latex	Skim Latex
Complete dispersion > 5.30	Complete dispersion > 6.50
Partial coagulation 5.30–4.62	Partial flocculation 6.50–5.83
Complete coagulation 4.62–3.31	Coagulation almost complete 5.83–5.28
Coagulation almost complete 3.31–2.51	Complete coagulation 5.28–3.53
Partial coagulation 2.51–0.73	Complete dispersion 3.53–1.00
Complete coagulation < 0.73	Complete flocculation 1.00–0.70
	Complete coagulation < 0.70

contains a small proportion of serum substances, while the skim fraction is of relatively low rubber content and contains most of the serum components. The samples used in the experiment were obtained by separation in a Sharples super-centrifuge of field latex, to which was added 1 per cent by volume of a solution

FRESH LATEX.

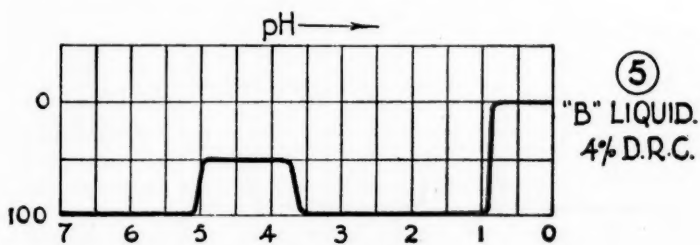
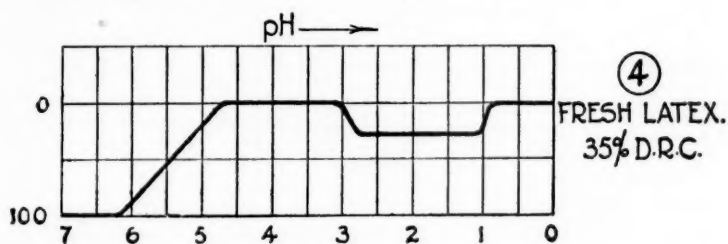
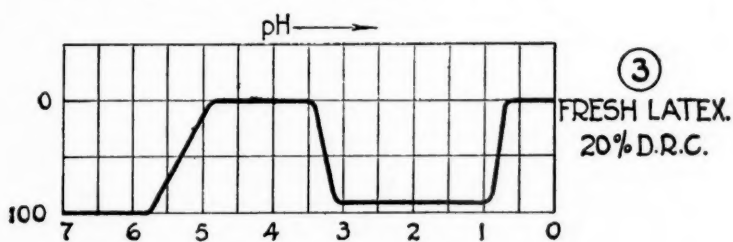
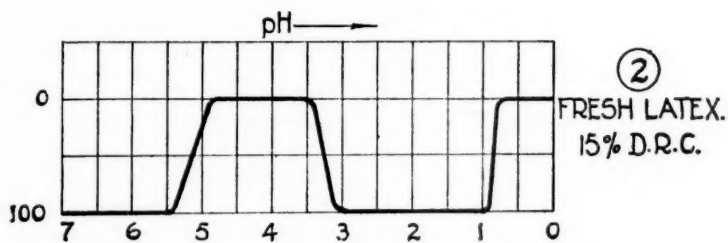
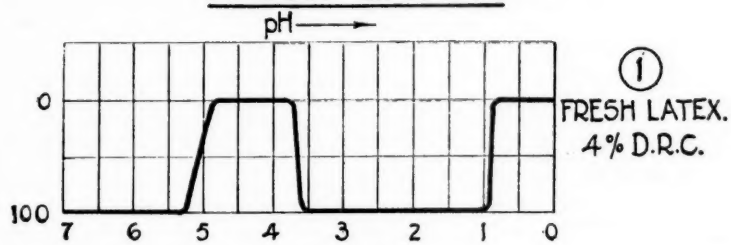
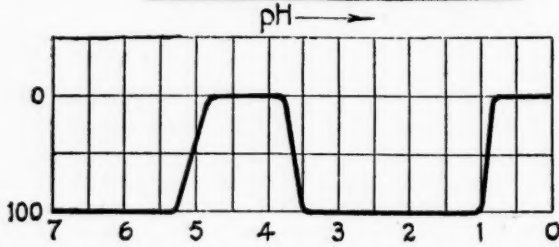
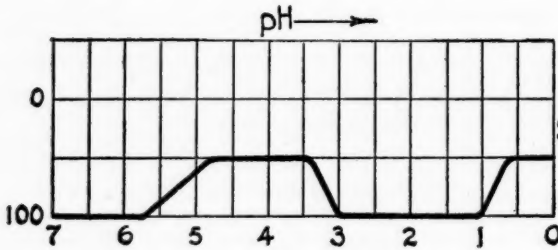


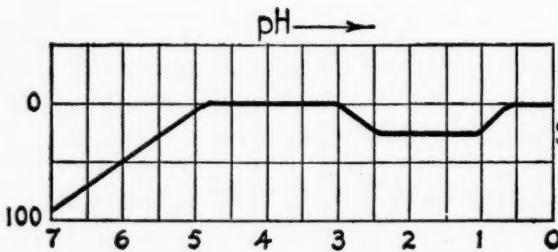
Diagram 2

PRESERVED LATEX

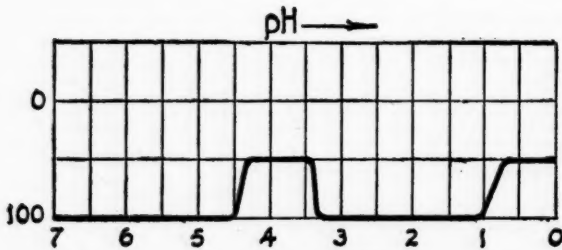
⑥
AMMONIA.
4% D.R.C.



⑦
FRESH
SODIUM HYDROXIDE
4% D.R.C.



⑧
LONG STORAGE
SODIUM HYDROXIDE
4% D.R.C.



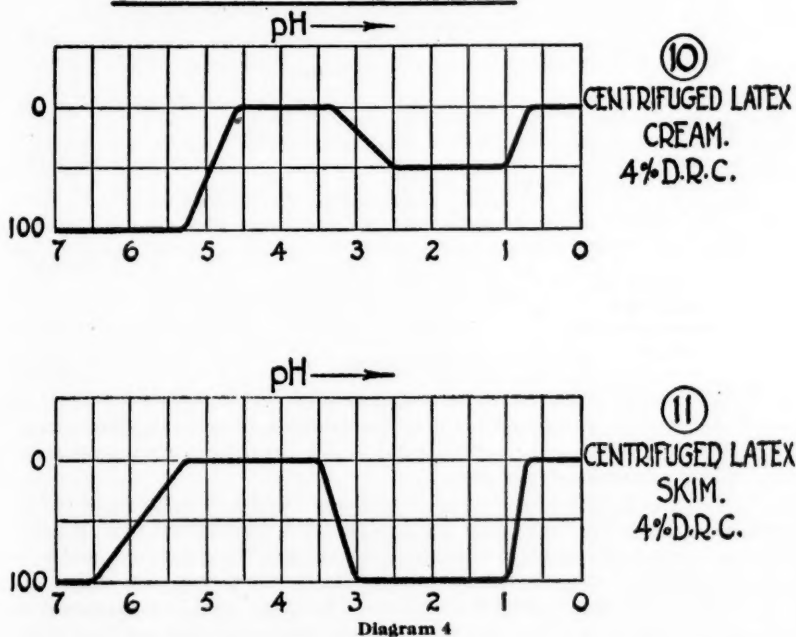
⑨
FORMALIN
4% D.R.C.

Diagram 3

of ammonia of 0.891 specific gravity. The cream fraction had a dry rubber content of 55.2 per cent and the skim fraction 10.3 per cent. It may be mentioned that this type of centrifuge was not found to be suitable for continuous work, though in the case under discussion separation was quite successful.

With the object of comparing the course of coagulation for these two fractions, each was diluted to a rubber content of 4 per cent and examined shortly after preparation. Table XVI, which summarizes the results obtained, shows that there is a considerable difference in behavior. With cream latex, there is no second liquid zone or zone of complete dispersion. Between p_H 2.51 and 0.73, slight clotting takes place, and about one-half of the total rubber present separates as a coherent clot. In behavior it is very similar to undiluted field latex having a rubber content of 35 per cent. With the skim fraction, however, there are two

CENTRIFUGED LATEX.



zones of complete coagulation separated by two zones of complete dispersion, and the first evidences of separation commence at p_H 6.50, at which flocculation sets in, whereas with cream latex coagulation commences at a lower value—viz., p_H 5.30. Skim latex is peculiar in that there is a flocculation stage in the passage from the second liquid to the second coagulation zone—the range p_H 1.00–0.70 defines a condition of complete flocculation. It will be noted that in all the preceding data cited for pure latex, the flocculation stage is associated only with the transition from complete dispersion to the first coagulation zone, and does not appear in the transitional stages between the other zones.

To summarize the experimental work described above, an attempt has been made to illustrate graphically in Diagrams 1, 2, 3, and 4 following a system which accords sufficiently well with the observed facts to bring out differences in the behavior of the various latices. For this purpose the results have been arranged

under three headings: (a) fresh latex, (b) preserved latex, and (c) centrifuged latex. To illustrate the course of the irregular coagulation series for a particular latex, the scheme adopted is to divide the abscissa into a scale of p_H values and to divide the ordinate into an arbitrarily chosen scale representing the degree of dispersion in the various stages. The number 100 is chosen to represent a state of complete dispersion, while zero represents a condition of complete coagulation. The scheme does not permit of numerical representation of conditions of the dispersion intermediate between these two extremes, but it does allow of comparison of the ranges of p_H values defining the various zones and roughly of the comparative degree of dispersion within these zones.

The effect of dry rubber content on the continuity of the course of coagulation for fresh latex is also summarized in Table XVII compiled from the experimental results recorded under Section A.

TABLE XVII
FRESH LATEX

State of Dispersion	Range of p_H			
	D.R.C. = 4 %	D.R.C. = 15 %	D.R.C. = 20 %	D.R.C. = 35 %
Complete dispersion.....	>5.30	>5.54	>5.80	>6.24
Partial flocculation.....	5.30-5.01	5.54-5.24
Complete flocculation.....	5.01-4.91
Partial coagulation.....	6.24-4.71
Coagulation almost complete.....	4.91-4.83	5.24-4.78	5.80-4.84
Complete coagulation.....	4.83-3.80	4.78-3.51	4.84-3.51	4.71-3.02
Coagulation almost complete.....	3.80-3.52	3.51-3.01	3.51-3.02	3.02-0.83
Complete dispersion.....	3.52-1.00	3.01-1.23
Partial coagulation.....	1.00-0.82	1.23-0.73	3.02-0.60
Complete coagulation.....	<0.82	<0.73	<0.60	<0.83

Conclusions

1. The continuity of the course of coagulation of: (a) fresh field latex, (b) preserved latex, and (c) centrifuged latex, by the addition of acids has been studied, and the p_H values defining the various zones in the irregular series determined by means of the quinhydrone electrode.

2. In the case of fresh latex diluted to a rubber content of less than 10 per cent the transition from the first liquid zone to the first coagulation zone is accompanied by a progressive series of changes in the state of the dispersion, and is also rather irregular, variations in the p_H values defining the transitional stages being found for latex harvested on different days. In most cases on examining the series in the direction of decreasing p_H there is a gradual progression from a state of complete dispersion to complete coagulation, through regions of partial flocculation, complete flocculation, and incomplete coagulation in that order. Generally, the range covered by this transitional stage is from p_H 5.30, at which point a separation of the rubber component from the dispersion is first visible at p_H 4.87, which marks the beginning of complete coagulation. These values agree fairly closely with those obtained by van Harpen.²

3. The dry rubber content of fresh field latex exerts a marked influence on the course of the irregular series. With latices varying in rubber content from 4 to 35 per cent the range of p_H values defining the transitional stage between the first liquid and the first coagulation zones increases as the dry rubber content increases. On the other hand, with increasing rubber content the range of values defining a condition of flocculation decreases until with latices of a rubber content higher than approximately 15 per cent this stage disappears altogether. It was also found

that, with latices of between 20 and 35 per cent concentration, there is no second zone of complete dispersion. Whereas the dispersion of latices of greater dilution is complete in the range covered by the second liquid zone—approximately p_H 3.5 to 1.0—and will remain stable for several days provided the hydrogen ion concentration is kept constant, with latices of greater concentration than 20 per cent, coagulation takes place for approximately the same range of value, the extent of the coagulation depending on the rubber content.

4. Independent of the degree of dilution of fresh field latex, the appearance of a flocculation stage is associated only with the transition from the first liquid zone to the first coagulation zone.

5. The irregular series for boiled latex or "B" liquid was studied, and confirmation was obtained of observations made by other workers to the effect that such latex does not coagulate until a p_H value of 0.80 is reached and, moreover, that the addition of soaps such as sodium oleate restores normal coagulation in the first zone. This was compared with the effect of the addition of sodium oleate to fresh field latex diluted to the same rubber content as the "B" liquid. Measurement was made of the alteration in p_H which occurs in fresh latex heated to various temperatures and allowed to cool to the initial temperature.

6. As regards the course of the irregular series, it was found that latex preserved with ammonia behaves in much the same way as fresh field latex. In latex preserved with formalin, however, it was found that if the latex is diluted to a rubber content of less than 10 per cent, coagulation by acid does not occur for any value of p_H below 7.0. For approximately the same ranges of values within which fresh latex of the same dilution shows two well marked coagulation zones, there correspond two zones of complete flocculation in the case of formalin-preserved latex. Even when the latex is undiluted, coagulation by acid takes place only after mechanical kneading of the flocculated mass. The same behavior was noted for freshly prepared latex treated with sodium hydroxide. On the other hand when latex preserved with sodium hydroxide is stored for a month or more, normal coagulation is restored within these two zones, though the course of the series is almost continuous, there being no second liquid zone. In such latex also, clot formation by the addition of acids can commence at a p_H on the alkaline side of neutrality.

7. A study was also made of latex separated into "cream" and "skim" by centrifugal action. It was found that cream latex behaves in a similar manner to latex preserved with sodium hydroxide which has been stored for a month or more, in so far as there is practically no break in the continuity of the series. With the skim fraction on the other hand, the irregularity of the series is just as well marked as in the case of fresh field latex. These remarks apply to latices diluted to a rubber content of 4 per cent.

Acknowledgment

The writer desires here to record his appreciation of the valuable advice of his colleague C. F. Flint on the assembly of the apparatus used in these investigations.

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- ² *Archief voor de Rubbercultuur*, **13**, No. 1 (1929).
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- ⁶ *Archief voor de Rubbercultuur*, **8**, 233 (1924).
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The Lipin of Hevea Latex

E. Rhodes and R. O. Bishop

Introduction

The so-called "resins" of plantation Para rubber have been described by Whitby^{9, 10, 11} and Dekker,¹ but the isolation of fatty bodies from *Hevea* latex itself has received little attention.

From the physiological as well as the chemical and technological points of view, it is extremely important that our knowledge of these bodies be extended because, apart from a possible rôle in coagulation phenomena and possible effects on the inner properties of prepared rubber, our knowledge of the part played by phloem tissues and phloem secretions in the economy of the plant is very scanty. Although latex is the secretion of a very specialized phloem tissue, it offers almost unique facilities for chemical examination, and in the following pages a brief general account is given of a peculiar fatty constituent of *Hevea* latex. Belgrave and Bishop in their work on the serum products obtained by alcohol coagulation separated a waxy body in quantities too small to permit of detailed examination. The present work, initiated as a result of those observations, records the first steps which have been taken toward a better understanding of the nature of this substance. The investigations are a natural continuation of the series of latex studies carried out during and since 1923, and recorded in the *Malayan Agricultural Journal*.

Method of Preparation

Preparations are made daily as follows:

Latex is slowly poured into approximately $2\frac{1}{2}$ times its volume of rectified spirit. The rubber is removed and pressed and the remaining alcoholic serum quickly filtered through a coarse filter paper. The fresh filtrate is quite clear, but soon becomes opalescent on standing. The serum is then concentrated under reduced pressure at a temperature of 40° C. Higher temperatures cause a very pronounced darkening in the color of the liquid. When the liquid has been concentrated to approximately one-twelfth its original volume, distillation is suspended. The aqueous liquid now possesses a milky appearance, and after cooling is extracted with ether in a separating funnel. With the first fifty-two preparations it was not possible to carry out the ether extractions immediately, and the milky liquids were preserved for five or six days at a temperature not exceeding 10° C.

Under these conditions the milkiess of the liquid disappears and a sweet smelling, buttery substance rises to the surface. Ether extraction removes the opalescence or the scum, as the case may be, leaving a small amount of flocculent solid matter suspended in an otherwise clear liquid. Three extractions with ether usually suffice to remove the ether-soluble material, but it is necessary to exercise care to avoid the formation of emulsions which are very slow in breaking. The combined ether extracts containing the fatty component are evaporated quickly to dryness at room temperature and finally dried in a vacuum desiccator. The product is a solid, transparent, golden yellow substance with a rather waxy feel and an earthy taste. Small quantities of the substance are prepared daily and when a suitable number of small preparations have accumulated, they are re-

dissolved in ether and bulked. The ether is removed and the resulting bulk is dried in a vacuum desiccator and weighed. It is thus possible to obtain an idea of the amount of substance obtainable by this means from a given quantity of latex. In Table I the figures are given for the first four bulked samples. The latex used in these experiments was obtained from the same block of trees situated at the Department of Agriculture, Kuala Lumpur.

TABLE I

Sample No.	No. of Samples Bulkcd	Daily Samples Prepared in 1930 between	Total Volume of Latex Employed, Cc.	Total Wt. of Ether Soluble Product, G.	Wt. of Product per 100 Cc. Latex, G.
I	15	May 29 and June 30	19,700	45.7	0.232
II	11	July 1 and July 17	15,300	36.0	0.235
III	11	July 18 and Aug. 1	16,200	34.4	0.212
IV	15	Aug. 5 and Aug. 26	21,600	35.6	0.165
Totals	52	May 29 and Aug. 26	72,800	151.7	0.208

It will be observed that the yield is approximately 0.2 per cent, calculated on the latex. This figure is much lower than the values obtained by Dekker¹ by hot acetone extraction of smoked sheet, which were 4 per cent on the dry rubber, representing approximately 1.4 per cent on the original latex. The method of cold extraction in an alcohol-water mixture adopted in our experiments could not possibly result in an exhaustive removal of the so-called "resins," and can only be expected to remove such bodies as are very readily dispersible in water or alcohol and which are more of the nature of lipins than true fats or fatty acids.

General Physico-Chemical Properties

The substance obtained is very readily dispersible in water. When an ether solution is rubbed in a mortar with distilled water and the ether removed, there remains a permanent milky suspension with a slightly yellow tinge. The suspension resembles a soap solution forming foam and bubbles on agitation. From such a suspension it is practically impossible to re-extract the substance with ether. In one experiment the attempt was made to wash the substance with water to free it from possible inorganic impurities. It was suspended with water in a separating funnel and ether was added. Even very slight agitation caused the dispersal of the ether into the aqueous medium from which it could not be induced to separate. Even after fourteen days the separation was only just commencing.

When a small quantity of the solid is treated with a drop or two of water and left for some hours, the material assumes the form of a jelly. If the early stages are observed under the microscope, small, round globules can be seen detaching themselves from the main mass floating away into the water. Myelin forms do not appear to occur.

The substance has a pronounced effect on surface tension. An emulsion in distilled water was prepared, having a concentration of 0.2 per cent, which imitates what appears to be its concentration in latex. The surface tension measured by a Du Nuoy ring testing apparatus was approximately one-half that of distilled water. Stronger suspensions produced greater reductions in surface tension.

The substance can be flocculated from a water emulsion by the addition of acids. A 2 per cent suspension in distilled water had a p_H value of 5.8, measured by the quinhydrone electrode. The addition of a small quantity of mineral acid produced a distinct color change, the emulsion becoming distinctly whiter in color, but with no pronounced change in stability. With the addition of increasing

quantities of acid, the color became progressively whiter, and when a p_H value of 2.5 was reached, there were distinct signs of the formation of curds. At a p_H value of 1.9–2.0, the suspended material was precipitated in large curds in a water-clear liquid. The curds were still soluble in ether and extraction was quite easy. The tendency to form emulsions seemed to have largely disappeared. The apparently complete flocculation can be brought about with any of the strong mineral acids and with formic acid, but not with acetic acid.

In a similar manner an apparently complete flocculation is produced by the addition of a little calcium chloride or magnesium chloride, and in both cases the flocculated material is soluble in ether.

General Chemical Properties

The substance has no definite melting point. When heated to 60° C. it softens slightly, but does not melt. When heated over a free flame it melts and chars at the same time, giving off first a smell like hot lard and finally cokes badly, smelling like burnt sugar.

When a little of the dry material is treated with concentrated nitric acid there is a very striking color change. The mass immediately assumes a bright cherry-red color. The solid matter breaks up and the acid liquid assumes the red color. On standing for some little time a dark red oil comes to the surface leaving a clear liquid below. If the liquid is heated, nitrous oxide is evolved, and the red oil disappears to be replaced by yellow oil drops which solidify to form a bright yellow waxy body, soluble in ether and warm alcohol.

In common with the cerebroside, it gives a deep purple-red color when rubbed with concentrated sulfuric acid, and this color is produced very quickly in presence of a little cane sugar.

The substance gives a strong Molisch reaction. Protein tests are negative.

The iodine number of the original material is 97. If an aqueous suspension be made, flocculated with acid, and the precipitated material extracted with ether, it is found that approximately 95 per cent of the original weight of material has been recovered. The loss in weight is due in the main to the loss of inorganic constituents. The iodine value of the ether-extracted material is now found to be 102, and the increase from 97 corresponds to the loss of 5 per cent of material having no iodine value.

Ether Soluble Phosphorus and Nitrogen

The various bulk preparations all contain nitrogen and ether soluble phosphorus, and all have a fairly high ash content. The precise amounts of each in the different bulked samples are very similar. Table II gives the values obtained. Nitrogen was estimated by the Kjeldahl method and phosphorus by Neumann's gravimetric method as magnesium pyrophosphate.

TABLE II

Bulk	N, %	P, %	Ash, %	N/P Ratio
I	0.59	1.72	5.35	1:1.32
II	0.58	1.67	5.74	1:1.30
III	0.55	1.45	5.49	1:1.19
IV	0.54	1.59	4.60	1:1.33

These figures, while suggestive of the presence of lipins, indicate that if such be present they are not by any means in a state so pure as is attained with animal phosphatides, since, for a pure phosphatide such as lecithin, the nitrogen and

phosphorus contents would be approximately 1.8 and 4.0, respectively, while a pure cerebroside would similarly require 1.8 per cent of nitrogen and no phosphorus.

It is customary to calculate the amount of phosphatide from the formula—lecithin (per cent) = P_2O_5 (per cent) \times 11.37—so that the substance of Sample I

should contain $\frac{1.72 \times 142 \times 11.37}{62} = 44.8$ per cent of phosphatide. Now since

the phosphatides are insoluble in acetone, some 44.8 per cent of the bulk of the fat should be insoluble in acetone but soluble in ether. A known weight of dry substance (6.40 g.) was extracted with six successive lots of warm acetone. The residual insoluble material was treated with ether. It gave a solution which was very slightly opalescent. This on filtration became quite clear, and the final yield of acetone-insoluble, ether-soluble material was 2.666 g., i. e., 41.7 per cent of the whole. This material when subjected to analysis gave the following figures:

N, %	P, %	N/P Ratio
0.88	2.56	1:1.31

These figures indicate that this fraction, though present in the expected amount, does not consist at any rate of a pure phosphatide, though the amounts of ether-soluble phosphorus and nitrogen show a decided increase and retain the same mutual ratio.

Fat Constants

The original substance has an acid value of 14, and an ester value of 159, giving a true saponification value of 173. The quantity of unsaponifiables soluble in ether is 1.1 per cent and the yield of ether soluble acids is 71 per cent of the original weight of material. Now a true fat would give a much higher saponification value, even if its constituent acids were of high molecular weight, and a yield of acids in the region of 90 per cent. A wax would give a low saponification value but a high unsaponifiable content. The low value obtained for unsaponifiable matter excludes a high content of wax. A true phosphatide yields 70 per cent of its weight of fatty acids, but it has been shown that the substance is not a pure phosphatide of the lecithin type. The figures thus indicate the presence of some substance which is not normally a component of fats, waxes, or of pure animal phosphatides.

Fatty Acids

When the mixed acids obtained by alkaline hydrolysis were subjected to separation by the lead salt-ether process into their solid and liquid constituents, it was found that liquid acids constituted practically the whole. The amount of solid acids was 5 per cent, the remaining 95 per cent falling into the category of liquid acids. Determinations of the iodine values of the two fractions showed that, as is often the case, separation had not been perfect. The values were:

Liquid acids	123
Solid acids	59

The solid acids were quite white and hard. The liquid acids, when brominated in the usual manner for the determination of the hexabromide value, yielded a little ether-insoluble bromide (1.924 g. of liquid acids gave 0.043 ether-insoluble bromide), which calculated as a percentage on the weight of acids gives a value of 2.5 per cent for possible hexa- and octabromides. When the ether-soluble bromides were submitted to semi-quantitative separation by petroleum ether into

soluble and insoluble fractions, the presence of a large proportion of acids belonging to the linoleic series was indicated. Dekker¹ isolated from smoked sheet liquid acids having an iodine number of 131, which is in agreement with the figure obtained in our experiments.

In order to test whether resin acids proper, as distinct from fatty acids, were present in the mixed acids, a known quantity of mixed acids were subjected to alcoholysis by Twitchell's method. The acids in solution in absolute alcohol were treated with hydrochloric acid gas until saturated. By this means the fatty acids but not the resin acids would be esterified. After cooling, and dilution with water, the liquid esters and resin acids were extracted with ether, the ether solution washed until free from acid and diluted with alcohol. Titration with standard alkali gives a measure of resin acids. The mixed acids were found to be 97 per cent esterifiable, and since this method always gives high results for resin acids, it may be taken that resin acids proper are present only in negligible quantity and that the mixed acids consist of true fatty acids.

Sugar, Possible Bases, and Glycerol

Using a small quantity—about 4 grams—of the material, an attempt was made to obtain by alcoholysis a solution containing any bases in a condition suitable for the application of qualitative tests. The crude material was treated with absolute alcohol, in which it was not, however, completely soluble, and dry hydrochloric acid gas was passed through the liquid until saturation was reached. By this time the liquid was very dark brown in color. The flask was heated under a reflux condenser on the water bath for five hours. As heating proceeded, the liquid became quite black, and humus bodies began to be formed. After removing alcohol and adding water, the esters appeared as a dark oil on the surface of the acid aqueous liquid. Esters were removed by extraction with ether and humus bodies by filtration. The aqueous liquid was made up to a known volume and parts of it were used for various tests. The appearance of humus bodies, in the known absence of proteins, had already given the clue that hexose sugars must be present in the original material and undergoing decomposition by heating in the strongly acid solution. The aqueous liquid reduced Fehling solution very readily, and gave a crystalline osazone which, when examined under the microscope, was found to consist of small somewhat irregular shapes such as are given by galactose and sometimes maltose. It is not yet possible definitely to name the sugar, but its existence in every sample since treated has been ascertained by the osazone reaction. When an aliquot part of the aqueous solution was estimated for sugar by the reduction of Fehling solution, and the value for hexose calculated on the original weight of material, a figure of 12 per cent was obtained, but little reliance can be placed upon it in view of the very drastic decomposition which had taken place, with the probable appearance of reducing bodies other than sugar. The development of humus bodies should coincide with the appearance of levulinic acid. The aqueous liquid was found to contain a body which readily gave the iodoform reaction in the cold, which is one of the characteristics of levulinic acid. The usual precipitants for bases, mercuric chloride, platinum chloride, and picric acid, applied in alcohol solution, and phosphotungstic acid, all give precipitates readily, and the Florence test with KI_3 was positive. The material precipitated by phosphotungstic acid, when analyzed for nitrogen, and referred to the original weight of fat, indicated that 71 per cent of the total nitrogen had been so precipitated. The evidence thus indicates the presence of a base of which the nature is as yet unknown.

A part of the liquid was treated with freshly prepared bromine water to oxidize

any glycerol to dihydroxy-acetone, which when dehydrated to methylglyoxal by sulfuric acid gives color reactions with alcoholic solutions of (a) salicylic acid and potassium bromide, (b) resorcinol, (c) thymol, and (d) β -naphthol. These tests were positive. The acrolein test was applied to a little of the original material. The actual smell of acrolein was masked by that of burnt sugar, but the vapors were strongly irritating to the eyes and throat, indicating the probable presence of acrolein. The evidence so far obtained thus favors the presence of glycerol, but it will be necessary to work with larger quantities of material before its presence or absence can be definitely proved and its amount estimated.

The Occurrence of the Sugar

In the first hydrolysis of the material by alcoholic potash, a sticky substance was observed to be precipitated during saponification. Later, when the alcohol was removed and water was added for the purpose of extracting unsaponifiable matter, this body dissolved quite readily and did not interfere in any way with subsequent treatments. The aqueous liquids after removal of unsaponifiable matter and fatty acids were neutralized before evaporating to small bulk for examination. These liquids were tested for the presence of reducing substances, but always failed to reduce Fehling solution. After having definitely noted the presence of reducing sugar in the products of acid hydrolysis, further samples of material were submitted to alkaline hydrolysis, and the sticky material which was precipitated during saponification was separated from the alcoholic liquid by decantation. After washing with absolute alcohol, and combining the washings with the original alcoholic potash, the alcohol-insoluble body was made up to a known volume with water, in which it readily dissolved. This solution was found to contain 98 per cent of the total phosphorus present. This might have been predicted since the alkali phosphates are practically insoluble in alcohol. The aqueous liquid did not reduce Fehling solution. It was found, however, that if the solution were heated with 10 per cent of hydrochloric acid for some little time and then neutralized, it reduced Fehling solution readily, and gave an osazone exactly similar to that previously obtained by acid hydrolysis. The amount of hexose was 8 per cent of the whole, when estimated by the reduction of Fehling solution, and calculated as a percentage of the amount of the fatty body. The saponification liquid after removal of alcohol, addition of water, precipitation, and removal of fatty acids, smelt strongly of sugar, and after inversion with hydrochloric acid, itself reduced Fehling solution. The amount of hexose present in this liquid was 1.6 per cent, which would give a total of 9.6 per cent for the total hexose present. This value is lower than that obtained previously, but it has since been shown that the whole of the sugar is only split off with some difficulty. Further it would appear that the sugar is not present originally as a reducing sugar. In a subsequent experiment, a known weight of the body was dispersed in water and treated with 10 per cent of hydrochloric acid. It flocculated immediately, and the suspension was heated to boiling over a free flame, until a stage was reached when the curds appeared quickly to reduce in volume and rise to the surface. Heating was then stopped, and after removal of the suspended matter with ether, the acid liquid was found to contain an amount of hexose equivalent to only 3.6 per cent of the original weight of material. It has since been found that in such an acid hydrolysis in an aqueous medium, if heating be continued after the stage when the curds appear to change in consistency, they eventually undergo a further change and form a definite oily layer at the surface and the reducing power of the liquid is now very much greater.

In another experiment, a quantity of the material was dissolved in ether, poured

into distilled water and warmed on the water bath at 70° C. to remove the ether leaving a uniform dispersion. This was flocculated by the addition of excess dilute hydrochloric acid and the flocculated matter extracted with ether. The aqueous liquid was preserved, and the ethereal solution which would contain a little acid, poured into a fresh lot of distilled water. The ether was again removed by heating on the water bath, leaving a very white dispersion from which a little solid matter settled out after some hours. The suspended matter was again removed with ether and reemulsified on the water bath as before. The suspension this time behaved like a thick flour paste, but dilution with water after some hours' standing showed the presence of innumerable small flocks. The extraction and redispersion was carried out five times, the emulsion being allowed to stand for some hours in each case, before being extracted with ether. At the fifth attempt no smooth dispersion was possible. The material was still not oily, but it consisted of flocks large enough to be incapable of dispersion. Examination of the aqueous liquids remaining at each stage showed that at the first flocculation the material lost a large proportion of its ash components. Subsequently a little more was lost at each stage. Sugar was similarly lost at each stage, together with some phosphorus and nitrogen. It is notable that the amount of phosphorus lost at the first flocculation is much smaller than in succeeding ones. The material remaining when dispersion had become impossible still contained an appreciable amount of phosphorus and nitrogen, but practically no ash. The total loss in reducing sugar estimated at each stage amounted to 10 per cent of the original weight of the material. There is a decided loss in freedom of dispersion after the first flocculation when the greater part of the ash components are removed. Subsequently the decrease appears to be gradual, with the loss of sugar at each stage.

Discussion

Sufficient evidence has been obtained to show that the material under examination is a peculiar complex of fatty acids, sugar, ether soluble phosphorus, and nitrogen, and possessed of properties abnormal to fatty bodies other than the ill-defined class called lipins. It is of considerable interest to compare some of the available facts with those adduced by other workers in the field of plant lipins. Maclean² has observed that the difficulties of investigating plant lipins are much greater than with similar products from animal organs, and that the difficulties are chiefly due to the presence of large amounts of carbohydrate material tending to form physical complexes similar to the "jecorin" bodies found in the animal world. Schulze and Winterstein⁷ pointed out that plant phosphatides contain considerably less phosphorus and nitrogen than the theoretical amount for lecithin. Winterstein and Hiestand¹² showed that plant phosphatides yield on hydrolysis sugar, as well as the usual decomposition products of phosphatides. The sugar content could be as high as 16 per cent. Specimens yielding large amounts of sugar generally yielded low phosphorus values. The sugars present can be in part removed by repeated washing with water, but various authors have produced evidence that some of the sugar is in chemical combination, since long boiling with acid is necessary to remove it. Maclean² says "there is no evidence that any observer has succeeded in obtaining from plants a carbohydrate-free lecithin similar to the substance found in animal tissues and organs." Among the "jecorin" substances of the animal world, some have been found which do not reduce Fehling solution directly. Offer⁴ and others have supplied such evidence, and Manasse³ and Sakaki^{5,6} describe jecorins which only reduce after long boiling with acid. The evidence provided by previous workers in the field of plant lipins provides a striking parallel to the present work and leaves little doubt that the material

from *Hevea* latex, while no more a pure phosphatide than any plant lipin previously described, can by virtue of its behavior and chemical composition be described as a plant lipin.

It is interesting also to note that by expressing the observed amount of phosphorus as glycerophosphoric acid, the nitrogen as choline, and ash as potassium oxide, a very interesting summation of constituents can be made.

	Per Cent
Phosphorus found, expressed as glycerophosphoric acid $1.72 \times \frac{172}{31} =$	9.55
Nitrogen found, expressed as choline $0.59 \times \frac{129}{14} =$	5.06
Unaponifiable matter found	= 1.10
Fatty acids found	= 71.00
Sugar found	= 10.00
Ash expressed as K_2O (found 5.35% ash)	= 3.55
	<hr/> 100.26

It may be argued that the calculations for nitrogen and phosphorus are not strictly justified, but since each of the elements must occur in some form of combination, it is at any rate reasonable to employ calculations for which there is some basis of evidence, and it is of interest to find that by such means it is possible to account for the whole of the material. Such a conception of its composition would allow for the presence of free fatty acids, some fatty acid soap as well as for fatty acids united to sugars, all of which seem necessary to explain the behavior of this peculiar complex.

With the accumulation of larger quantities of material, it is hoped to isolate the various constituents in reasonably large amounts and definitely to establish the identity of those about which some uncertainty at present exists.

Summary

A body having properties and composition similar to those of the plant lipin complexes described by various authors has been isolated from *Hevea* latex.

Acknowledgment

The authors' thanks are due to B. J. Eaton for his interest and encouragement in the progress of the investigations, and to K. C. Sekar for his assistance in many of the operations involved.

Note

Since writing the above we have received Van Harpen's⁸ recent publication dealing with the flocculation and coagulation of *Hevea* latex. In this publication some doubt is cast upon the validity of the theory of Belgrave because the lecitho-sugar complex which he postulated in 1923 had not up to the present been isolated. Since the phosphatide-sugar complex has now been isolated from fresh latex it becomes obvious that the theory originated by Belgrave assumes new and added significance.

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Observations on the Effect on Vulcanization of the Lipin of Hevea Latex

B. J. Eaton, E. Rhodes, and R. O. Bishop

Some preliminary vulcanization tests which have been made with the *Hevea* lipin (*vide Quarterly Journal of the Rubber Research Institute of Malaya*, 2, 125 (1930)) are described.

As already shown by one of the authors,¹ the rubber derived from alcohol-

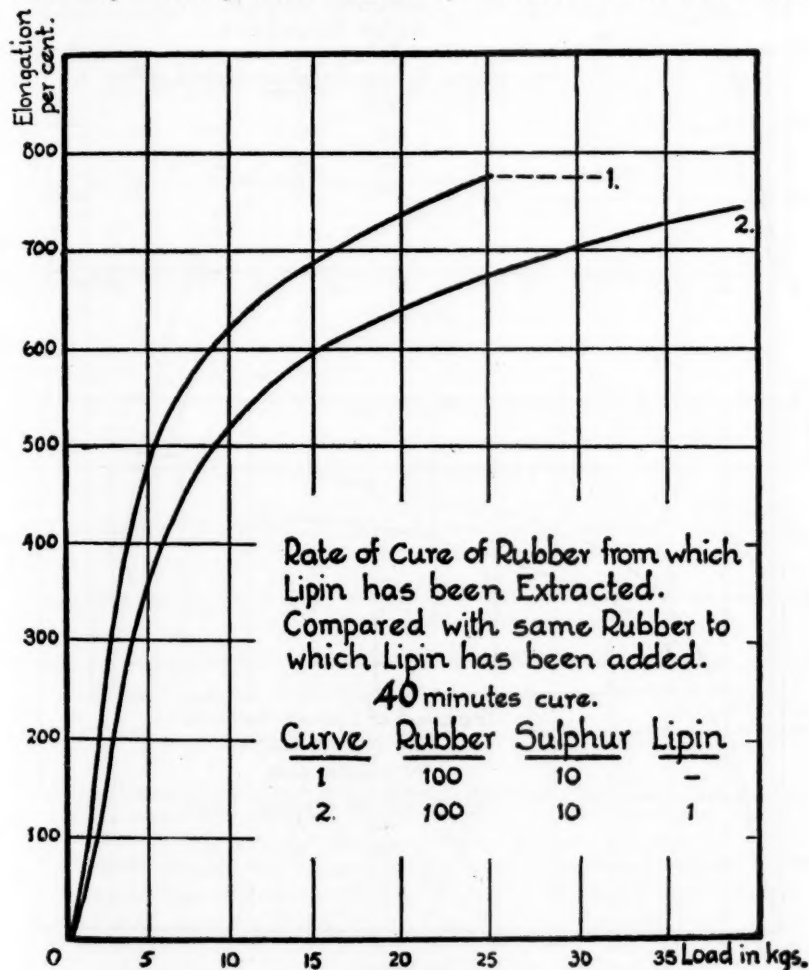


Figure 1

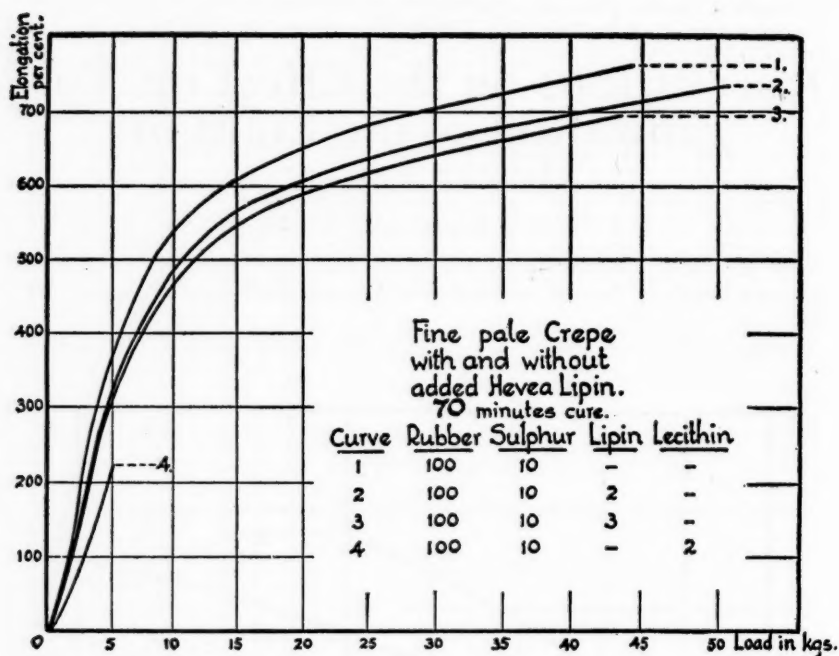


Figure 2

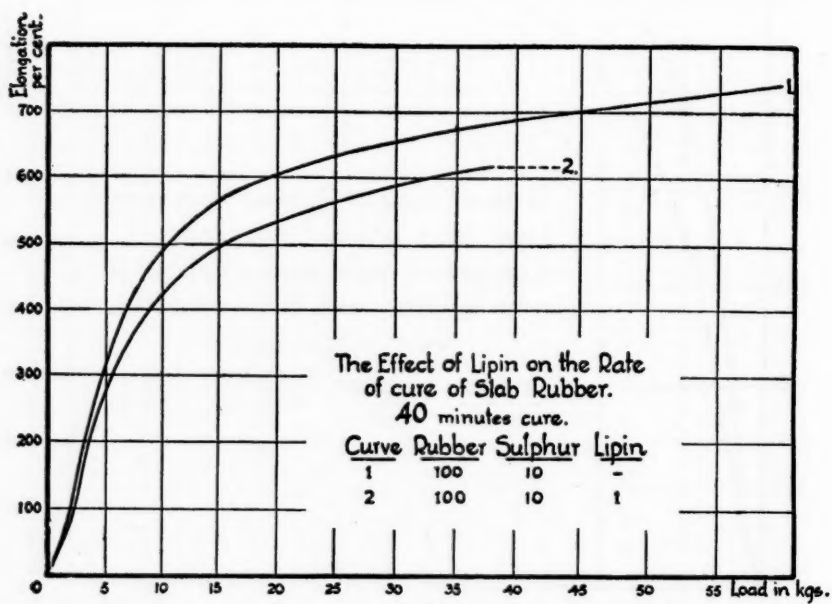
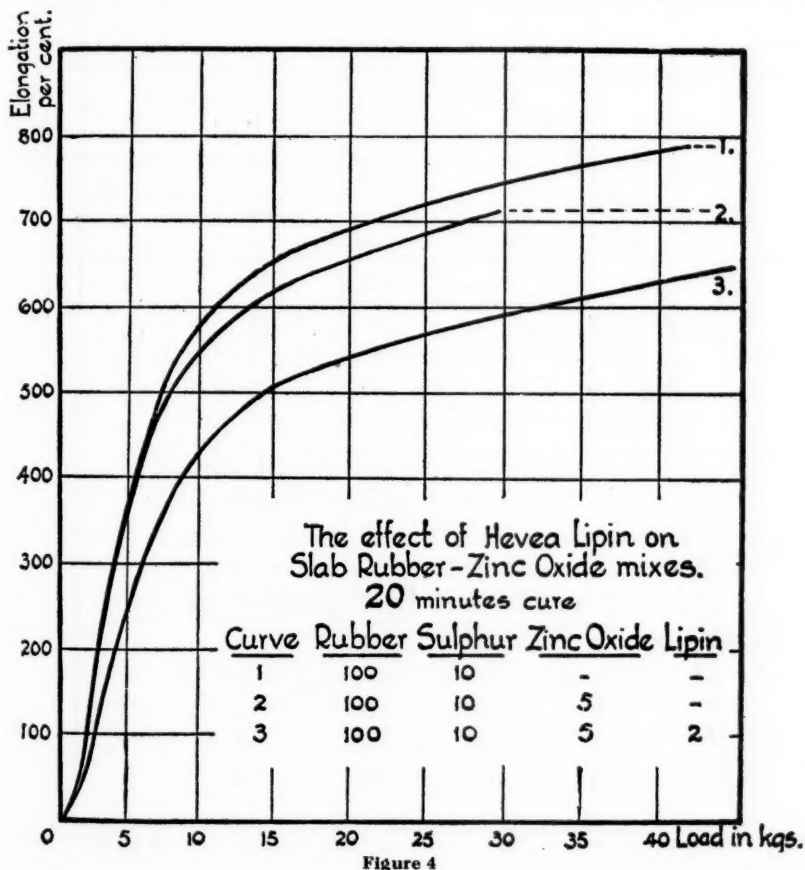


Figure 3

coagulated latex exhibits a much faster rate of cure than crepe prepared by the orthodox method of acid coagulation. In the present investigation it has been found that the alcohol coagula on pressing and drying give a rubber which shows an optimum cure at 60 min. compared with 90 min. for plantation crepe vulcanized under the same standard conditions in a mix consisting of 100 parts of rubber plus 10 parts of sulfur cured in a steam autoclave at 148°C . It is thus somewhat slower in rate of vulcanization than "slab" rubber, and approximately equivalent to "fine hard Para."

It has been found that the rate of vulcanization of this alcohol-coagulated rubber



prepared from different days' crops of latex shows practically no variation. Differences in detail of preparation, such as length of time of soaking in alcohol, dilution of alcohol, and period of drying of the coagula are insignificant.

The tensile strength and other properties of the vulcanized product are normal.

All preparations of alcohol-coagulated rubber, to which the separated lipin has been returned, show a definite acceleration in cure. An addition of 1 per cent of lipin is proportionately more effective than 2 per cent, and 2 per cent is proportionately more effective than 3 per cent, but there is acceleration in all cases which

is of the same order as that exhibited when the lipin is added to slab rubber (Fig. 3).

When the separated lipin is added to simple mixes containing only sulfur and normal plantation rubber, its effect varies according to the rate of vulcanization of the rubber. With fine pale crepe, which under our standard condition of vulcanization has an optimum cure of 100 minutes, the addition of *Hevea* lipin in the

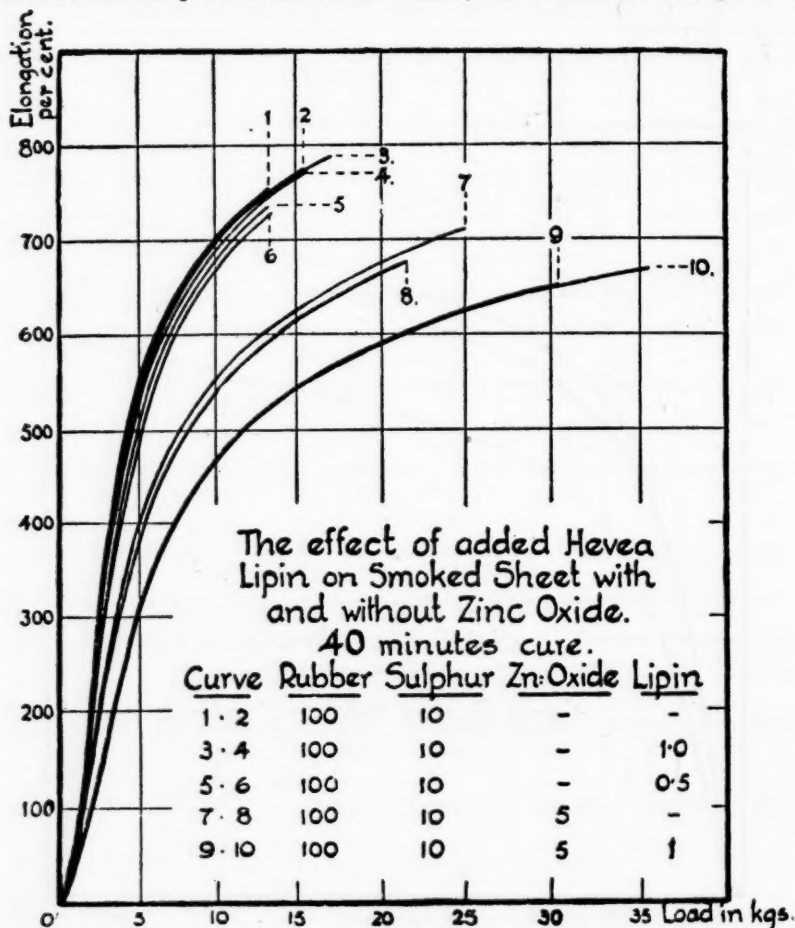


Figure 5

proportion of 1 per cent on the rubber causes no appreciable acceleration, while the addition of 2 per cent accelerates by 10 minutes (Fig. 2).

By contrast, if 1 per cent of the *Hevea* lipin is added to normal "slab" crepe, which under our standard conditions has an optimum cure of 40 minutes, an acceleration of 10 minutes is produced (Fig. 3).

Mixes containing 5 parts of zinc oxide per 100 parts of rubber show a greater acceleration for the addition of 1 per cent lipin than corresponding rubber sulfur mixes with and without zinc oxide, and in normal plantation crepe the degree of

acceleration is enhanced to such an extent that the optimum cure is almost as rapid as that obtained for a similar mix containing slab rubber (Figs. 4, 5, and 6).

It will be seen from a comparison of Figs. 2 and 6 that the rate of cure for the crepe is increased so much that the cure at 20 minutes (Fig. 6) is more complete than that for 70 minutes in Fig. 2.

Effect of Lecithin

In view of the probable relationship between *Hevea* lipin and egg lecithin, their effects on vulcanizations were compared. When crude technical lecithin was

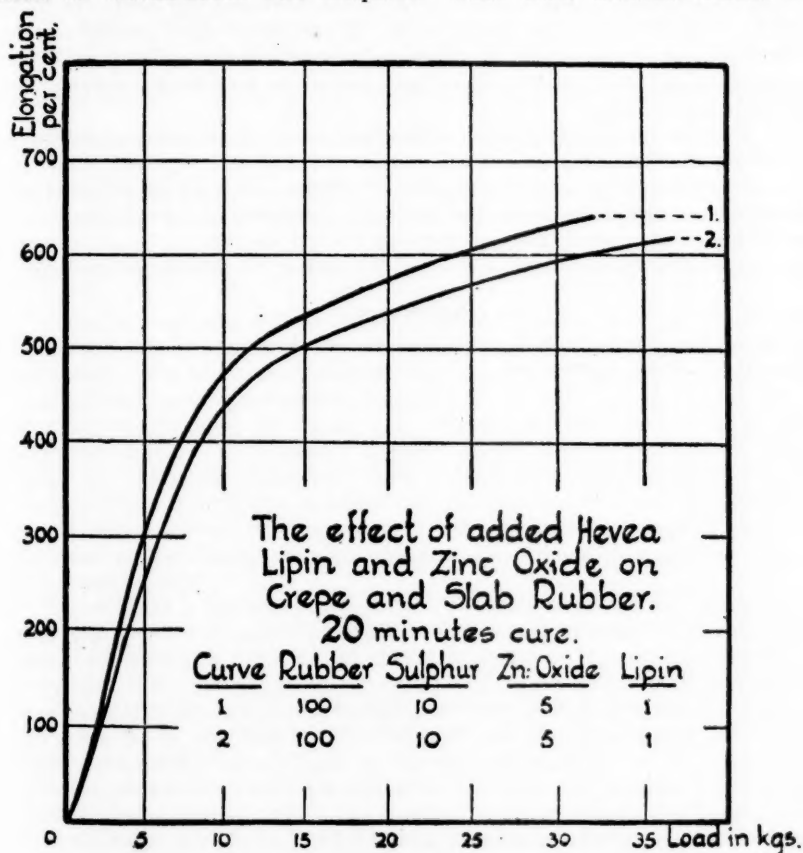


Figure 6

added to ordinary thin crepe rubber it was found that the degree of acceleration was materially greater than for *Hevea* lipin.

Effect of *Hevea* Lipin and Egg Lecithin on Rubber-Sulfur Mixes

It is interesting to note, however, that the effect of adding lecithin to rubber while mixing on the hot rolls is strikingly similar to that produced by *Hevea* lipin. Immediately the lecithin or lipin is added, the plastic mass becomes opaque and crumbles and resembles breadcrumbs. When the crumbling mass is subjected

to further mastication, though the temperature is not allowed to rise above 55° C., a further change takes place, and the mass again assumes the appearance characteristic of masticated rubber on the hot rolls.

The addition of small quantities of *Hevea* lipin or egg lecithin to raw rubber in the form of plantation crepe, smoked sheet, or slab crepe, is always accompanied by the same peculiar behavior during mastication on warm rolls. If, however, the rubber is first mixed with sulfur and/or zinc oxide, the degree of crumbling is considerably lessened, but the partially masticated mix shows a strong tendency to adhere to the rolls in spite of the fact that the mass feels distinctly greasy.

From the similarity in the behavior of the mixes containing egg lecithin or *Hevea* lipin, it is evident that we are dealing with a phenomenon related in some manner to the chemical characteristics of this class of substances.

From the preliminary work which we have carried out with the *Hevea* lipin, three important facts emerge:

(a) The peculiar physical effect of the lipin on the maceration properties of raw rubber on warm rolls.

(b) The acceleration of cure caused by the lipin in fast curing rubbers—slab and alcohol, coagulated—contrasted with the comparatively small effect on a slow curing rubber such as fine pale crepe or smoked sheet.

(c) The increased accelerating effect of the lipin in the presence of zinc oxide.

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The Structure Viscosity of Rubber Solutions

B. Dogadkin and D. Pewsner

INSTITUTE OF RUBBER INDUSTRY, MOSCOW, RUSSIA

On flowing from capillaries, rubber solutions show the deviations from the Hagen-Poiseuille Law which are peculiar to colloids. The measurement of the relative viscosity $\left(\eta_{rel} = \frac{T_k}{T_w}\right)$ of these solutions in the Ubbelohde viscosimeter showed, according to Kirchhof,¹ that with increase of pressure P the η_{rel} values diminish, whereby these values reach a definite numerical value which remains unchanged with further increase of P . Such a behavior of rubber solutions corresponds exactly to the general scheme suggested by Wo. Ostwald² for the functional dependence of the viscosity upon the rate of flow. This dependence can be represented by the following modification of the de Waele-Ostwald formula: $\eta_{rel} = K.P^{1-n}$.

In the de Waele-Ostwald equation, K and n represent constants which depend both upon the conditions of the measurement and on the properties of the liquid measured. The constant n depends chiefly upon the properties of the liquid, and its magnitude represents the extent of the deviation of the liquid from the Hagen-Poiseuille law. For small values of pressure P the constant n for colloids is greater than 1. Wo. Ostwald suggests designating the viscosities at these P values as "structure viscosity." Such a designation must be regarded as well chosen, since the deviation of colloids at low pressures from the Hagen-Poiseuille law is related to their polyphase internal structure and to change in the micellar structure of the colloids, which may take place even with insignificant changes in the rate of flow.

The constant n therefore characterizes the changes in viscosity occurring with change in pressure P , and in a certain sense this value can be considered as a measure of the structure of the colloid, that is, in this way there can be expressed both the extent of the mechanical effect of the micelles upon one another and also upon their mutual orientation, and the solidity of their internal structure. The numerical values for n , obtained by Wo. Ostwald³ and his collaborators, proved to be very characteristic for solutions of different substances.

In the present work we have endeavored to solve the problem to what degree the changes in viscosity within the so-called structure range, which are expressed numerically by n in the de Waele-Ostwald formula, can be utilized for distinguishing various kinds of rubber and for evaluating the changes which accompany the aggregation and disaggregation of rubber (for example, during milling and aging).

Data in the literature on the dependence of the viscosity η_{rel} of rubber solutions upon the rate of flow (or pressure P) appear in work by Kirchhof,⁴ Wo. Ostwald,⁴ experiments by Feldman, Iwanitzkaja and Herschel,⁵ and by Kroeplin.⁶ The first one of these established, as has already been referred to above, that rubber solutions at water-column pressures of 60 cm. and higher follow the Hagen-Poiseuille law. Consequently Kirchhof proposes measuring the viscosity of rubber solutions directly from these values of P , in order to work out a uniform procedure. It should be pointed out, however, that this suggestion does not exclude variations

in the results of individual measurements, because the η_{rel} values depend upon the radius of the capillary in the apparatus. Proceeding from hydrodynamic considerations, Haller and Trakas,⁷ as well as Kroepelin, derived an analytical formula for this relation. Stauf and others⁸ applied the de Waele-Ostwald formula directly to rubber solutions. The numerical values for n based on these experiments were in a series of colloids greatest in the case of rubber, and this agrees very well with our concept of the character of the internal structure of rubber.

I. Method

Our experiments were carried out in the ordinary Wilh. Ostwald viscosimeter which was combined with a water monostat, as described by Wo. Ostwald.⁹ The pressure in the monostat was expressed in cm. of a water column, and calculated by the formula $P = H + h\delta$, where H is the difference in level in the monostat, δ the density of the liquid, and h the difference in level in the viscosimeter. Since the variation in density of rubber solutions from the density of the solvent was insignificant, we used the numerical value of the solvent in all cases.

The length of time of the outflow of water (T_w) or of pure solvent (T_s), which is necessary in determining the relative viscosity, was determined graphically for different pressures P from the curves found by experiment. In the ideal case

TABLE I

Pale Crepe in Benzene Viscosimeter No. 1 $r = 0.049$ cm. $C = 0.5\%$				Pale Crepe in Benzene Viscosimeter No. 3 $r = 0.038$ cm. $C = 0.5\%$				Smoked Sheet in Benzene Viscosimeter No. 1 $r = 0.049$ cm. $C = 0.75\%$			
P	$\eta_{exp.}$	$\eta_{calcd.}$	$\Delta\%$	r	$\eta_{exp.}$	$\eta_{calcd.}$	$\Delta\%$	P	$\eta_{exp.}$	$\eta_{calcd.}$	$\Delta\%$
11.4	9.48	10.69	12.66	10.08	9.47	6.05		11.8	19.53	21.43	9.73
21.4	7.37	7.68	4.20	8.31	8.06	3.01		21.8	15.27	15.58	2.03
31.4	6.53	6.25	4.28	7.12	7.30	2.53		31.8	13.39	12.80	4.40
41.4	5.56	5.34	3.96	6.68	6.80	1.79		41.8	11.50	11.10	3.48
51.4	5.21	4.82	7.48	6.28	6.44	2.62		51.8	10.19	9.93	2.55
61.4	4.40	4.38	0.45	6.00	6.15	2.50		61.8	9.07	9.07	0.11
71.4	4.00	4.04	1.00	5.55	5.91	6.49		71.8	8.29	8.38	1.08
81.4	4.14	5.25		81.8	8.19
91.4	3.89	5.04		91.8	8.20
			0.24			0.98					0.33
	$n = 1.500$				$n = 1.352$				$n = 1.520$		
	$k = 38.85$				$k = 17.66$				$k = 77.35$		

of water and pure solvent $PT = K$, from which T_r can be calculated if K is obtained from a series of experiments. However, we found in our experiments with viscosimeter No. 1, having a capillary radius of 0.049 cm., that there were important deviations from the equation: $PT = K$. With viscosimeter No. 3, with a 0.038-cm. capillary for water, benzene, and toluene this formula was valid within rather broad limits of P (up to a 90-cm. water column). Strangely, chloroform showed an apparently constant deviation from the Hagen-Poiseuille law, and its relative viscosity increased with increasing values of P . Accordingly this solvent can only be used with caution in the study of the structure viscosity of rubber.

In determining the exponents of the structure viscosity, we applied the de Waele-Ostwald formula: $\eta_{rel} = K.P^{1-n}$. In this equation both constants, depend to a certain extent on the dimensions of the apparatus and the conditions of the experiment. Haller and Trakas (*loc. cit.*) changed the equation of de Waele-Ostwald so that both constants in the formula were independent of the external conditions, and appeared to be specific only for the liquid in question. However, in the application of this formula of Haller, difficulties were encountered on account of its complexity. For comparative experiments on the same apparatus, the constants of the structure viscosity in the de Waele-Ostwald formula can be regarded as a characteristic of the substance in question.

Converted into its logarithmic form, the de Waele-Ostwald formula is represented by the linear equation:

$$\log \frac{T_k}{T_w} = \log K + (1 - n) \log P$$

Figure 1 represents a curve of this equation for experimental data on solutions of smoked sheet and pale crepe. From Fig. 1 it is evident that the transition from the region of structure viscosity to the lamina region takes place in the range between P 70 and 90 cm. (water column). Therefore we proceeded to calculate the exponents of structure viscosity n from the data obtained from pressures which did not exceed 70 cm. The η_{rel} values calculated by the de Waele-Ostwald formula in these regions of P agreed with those found experimentally; the deviations did not on the average exceed 0.98% (Table I).

II. Structure Viscosity of Different Kinds of Rubber

It was to be expected that the peculiarities of different kinds of rubber would be expressed by their structure viscosity, and accordingly the exponent in the de Waele-Ostwald formula should show different values. In some cases this was

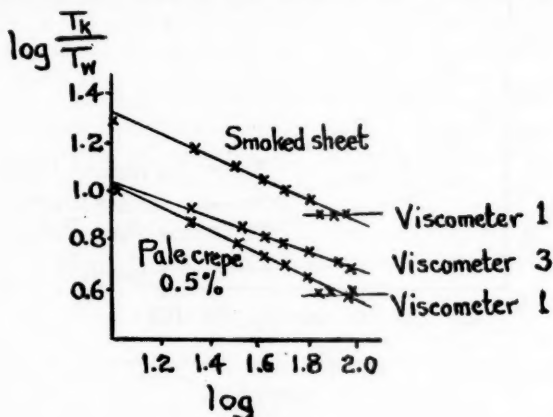


Figure 1

well suited to characterize disperse systems. Thus Nishikawa¹⁰ characterized the structure peculiarities of different kaolins by surfaces which were limited by the pressure-viscosity curve.

We carried out measurements of the structure viscosity for the following kinds of rubber: pale crepe, smoked sheet, Para and guayule. In preparing the solution the product was finely divided and agitated periodically for five to seven days. It is known that ordinary kinds of rubber are only partly dissolved in aromatic hydrocarbons under these conditions. The experiments were carried out with solutions containing no precipitate. Guayule passed into solution without residue, except for foreign impurities. The dried residue from decanted solutions was determined, after which the solutions were diluted to the necessary concentrations.

The experimental data prove that different solvents lying near one another in the homologous series have no marked influence on the structure viscosity of dissolved rubber. The constant n of the de Waele-Ostwald formula has very similar

values for a 0.5% solution of pale crepe in benzene, toluene, and xylene. The concentration of the solutions has a very great influence. With increase in concentration n also increased, which corresponds to a greater aggregation of the micelles in concentrated solutions. It is clear that the structure viscosity of the individual kinds of rubber can be compared only in solutions of the same volume concentration. We carried out these measurements with 0.4% and 0.75% solutions. Table II gives experimental data for the 0.75% solutions. Pale crepe, smoked sheet, and washed Para rubber are very similar to one another with respect to the character of their viscosity in the so-called structure region. Washed Para rubber had the greatest relative viscosity for all values of P . Pale crepe and smoked sheet were so similar in their relative viscosities that in Fig. 2 the changes in viscosity of these types of rubber are represented by the same curve. Nevertheless, in thirteen measurements out of fourteen, the pale crepe solution had a larger exponent of structure viscosity than the smoked sheet solution. We must conclude therefore that pale crepe shows a greater "measure" of structure in the

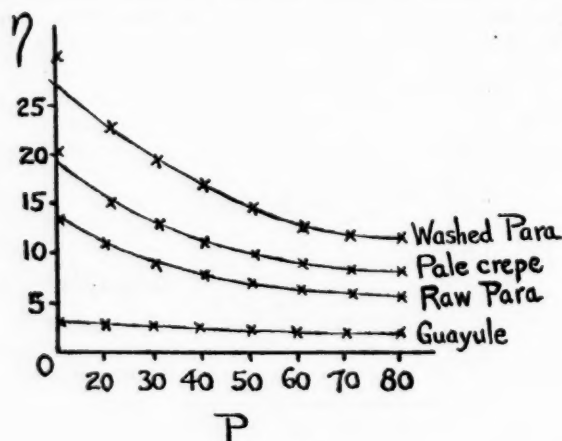


Figure 2

sense of Wo. Ostwald. We might also point out here that solutions of pale crepe appeared more stable in light to changes in viscosity than smoked sheet.

TABLE II

Solvent: Benzene; $t = 25^\circ$; r of the Viscosimeter = 0.049 Cm.

Pressure in Cm. (Water Column) P	Relative Viscosity $\eta_r = \frac{tk}{tw}$				
	Pale Crepe 0.75%	Smoked Sheet 0.75%	Para (Washed) 0.75%	Para (Raw) 0.75%	Guayule 0.75%
11.8	19.79	19.58	29.70	13.47	3.24
21.8	15.70	15.27	22.70	10.89	2.85
31.8	13.59	13.39	19.82	9.29	2.64
41.8	11.69	11.50	17.00	8.22	2.47
51.8	10.23	10.19	14.82	7.37	2.36
61.8	9.18	9.07	13.11	6.66	2.22
71.8	8.73	8.29	11.96	6.20	2.16
81.8	8.19	8.19	11.70	5.95	2.14
	$n = 1.527$	$n = 1.520$	$n = 1.550$	$n = 1.462$	$n = 1.232$

The types of rubber described above showed sharp differences in structure viscosity compared with guayule. With change of pressure, the change in viscosity of the solution was relatively insignificant.

If the kinds of rubber are arranged according to the exponent of their structure viscosity in the de Waele-Ostwald formula for 0.75% solutions, the following relations are found:

Para rubber (washed).....	1.550
Pale crepe.....	1.527
Smoked sheet.....	1.520
Para (raw).....	1.462
Guayule.....	1.232

To what extent this series corresponds to technical properties will be shown by further investigations.

III. Structure Viscosity as a Characteristic of Aggregation and Disaggregation Processes in Rubber

There is no doubt that changes in the internal structure of rubber brought about by various influences affect the structure viscosity. The problem of the structural changes of rubber is not sufficiently explained at the present time, and the terminology of the phenomena is rather confused. We will retain the terminology of Harries,¹¹ and understand by aggregation and disaggregation a purely colloid-chemical process of the change in dispersion of the rubber micelles.

The influence of heat on rubber is generally known. Through warming, changes can be brought about in rubber which are similar to those caused by milling. These changes influence the viscosity of rubber. Kirchhof studied the direct action of heat on the viscosity of solutions, and came to the conclusion that the relative viscosity of rubber solutions usually decreases with rise in temperature, while according to Kroeplin the viscosity remains unchanged in general with change of temperature.

TABLE III

Pressure in Cm. (Water Column) <i>P</i>	$\eta_s = \frac{\eta_k}{\eta_a}$ 0.5% Solution Pale Crepe in Benzene				$\eta_s = \frac{\eta_k}{\eta_a}$ Solution in Smoked Sheet in Benzene			
	<i>t</i> = 15°	<i>t</i> = 25°	<i>t</i> = 35°	<i>t</i> = 45°	<i>t</i> = 15°	<i>t</i> = 25°	<i>t</i> = 35°	<i>t</i> = 45°
11.4	12.95	12.55	12.54	12.12	11.5	11.06	10.80	10.65
31.4	8.72	8.48	7.88	7.54	7.84	7.65	7.06	6.83
51.4	6.90	6.91	6.04	5.66	6.24	6.08	5.50	5.14
71.4	6.00	5.29	5.52	4.60	5.50	5.11	4.70	4.63
	<i>n</i> = 1.424	<i>n</i> = 1.474	<i>n</i> = 1.478	<i>n</i> = 1.545	<i>n</i> = 1.415	<i>n</i> = 1.470	<i>n</i> = 1.487	<i>n</i> = 1.488

Table III gives our data for changes in viscosity at different temperatures between 15° and 45°. Here the viscosity is calculated for a solvent of $\eta_s = T_k/T_a$. This table shows that the viscosity of rubber solutions diminishes slowly but continuously with rise in temperature, while the exponent of structure viscosity calculated by the de Waele-Ostwald formula increases. There is a certain contradiction between these facts which can be explained by the fact that with increasing temperature the elasticity of the rubber micelles also increases. The increased capacity of the rubber micelles for deformation must be regarded as the result of this increase in elasticity. In any case, the measure of structure of rubber solutions increases at the higher temperatures.

Milling has a very great influence on the structure viscosity of rubber solutions. Pale crepe was milled on hot rolls at 60° and individual samples were tested for

their viscosity after standing for different periods of time. The measurement of the viscosity was carried out in a 1% benzene solution.

Even six minutes after the beginning of milling, the relative viscosity decreased noticeably, based on its absolute numerical values, and the viscosity curve which represents the dependence of the viscosity upon the pressure became less convex. The longer the time of milling, the more did the structural measure of the solutions diminish. After milling for thirty minutes, the internal structure of the rubber was so greatly broken down that a 0.7% solution gave only an insignificant deviation from the Hagen-Poiseuille law (Table IV, Fig. 3).

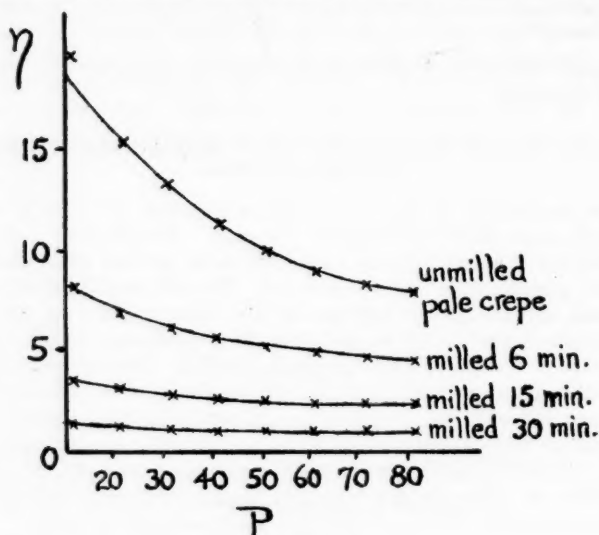


Figure 3

TABLE IV

Viscosimeter $r = 0.049$ Cm.; $t = 25^\circ$; Pale Crepe in 1% Benzene

Pressure in Cm. (Water Column) P	Length of Time of Milling in Minutes				
	Unmilled ^a	6 Minutes	10 Minutes	15 Minutes	30 Minutes ^a
11.8	19.79	8.48	5.01	3.66	1.64
21.8	15.70	7.04	4.37	3.21	1.46
31.8	13.59	6.51	4.24	3.07	1.42
41.8	11.69	5.88	4.03	2.88	1.41
51.8	10.23	5.47	3.70	2.75	1.31
61.8	9.18	5.11	3.44	2.52	1.29
71.8	8.73	4.79	3.25	2.46	1.25
81.8	8.19	4.71	3.24	2.48	1.29

$n = 1.527$ $n = 1.339$ $n = 1.279$ $n = 1.239$ $n = 1.153$

^a These solutions were in a 0.7% concentrated solution.

A difference in the behavior of milled and unmilled rubber was also observed in this fact that the relative viscosity η_{rel} of Kroeplin¹² is expressed by $8v/3r$. Here v is the average rate of flow and r the radius of the capillary in the viscosimeter. If milling does not injure the structural measure, the viscosity values for milled and unmilled rubber would be expressed by the same curve. As Fig. 4 shows, this is not the case.

These results show that, in milling, a colloid-chemical process of disaggregation

of rubber micelles is the chief phenomenon, and that there results a diminution of the structural measure of the solution. The processes of depolymerization (in the chemical sense of the term) accompany the disaggregation phenomena, and are probably brought about by the heat generated in the milling. We do not believe that Fry and Porritt¹³ are correct in asserting that the action of milling on rubber depends fundamentally on a chemical action of oxygen and a chemical depolymerization of rubber. These processes may take place, but they are to be regarded rather as secondary to the prolonged action of heating and when contact of rubber with oxygen is limited.

The structure viscosity is none the less greatly affected by the processes of aging of rubber. It is generally known that a sharp decrease in the viscosity of rubber solutions takes place on exposure to light and on heating in an atmosphere of oxygen, in other words, with all influences which bring about a natural aging of the rubber products. With the decrease in the absolute numerical value of the viscosity, the limits of change of viscosity under the influence of the pressure are correspondingly small, in other words, the structural measure of the solutions decreases. These facts were confirmed by measurements of solutions of smoked sheet and pale crepe after a month's exposure in the dark and in the light in tightly closed cylinders of white glass. The results of the experiments are given in Table V and Fig. 5. The viscosity of smoked sheet solutions was practically unchanged by the exposure in the dark, while the viscosity of a pale crepe solution diminished, as did the structural exponent n . On exposure to light, the behavior of these two

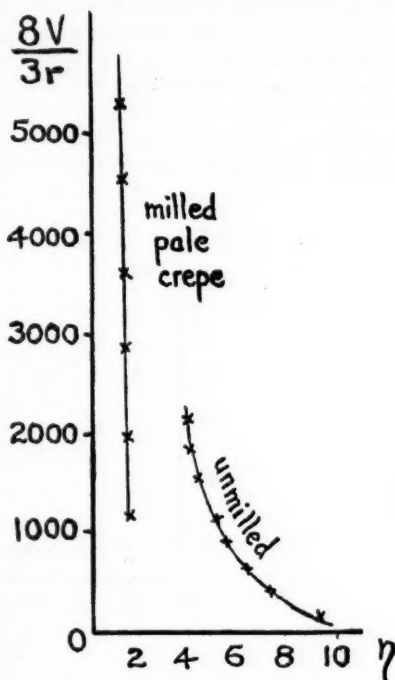


Figure 4

TABLE V
Viscosimeter $r = 0.049$; $t = 25^\circ$; 0.5% Solution in Benzene

Pressure in Cm. (Water Column) P	Relative Viscosity $\eta_r = \frac{I_k}{I_n}$						
	Pale Crepe before Aging	In Dark from 9.1 to 5.2	In Light from 9.1 to 5.2	Exposure to Ultra- violet Rays for 2 Hours	Smoked Sheet before Aging	In Dark from 9.1 to 5.2	In Light from 9.1 to 5.2
11.4	14.25	12.86	1.55	0.804	12.41	12.78	0.844
21.4	11.14	9.84	1.42	0.765	10.07	10.15	0.820
31.4	9.57	8.62	1.41	0.766	8.66	8.91	0.844
41.4	8.19	7.45	1.34	0.780	7.45	7.61	0.821
51.4	7.24	6.72	1.31	0.754	6.68	6.88	0.852
61.4	6.40	5.92	1.27	0.781	5.81	6.09	0.818
71.4	5.71	5.51	1.24	0.795	5.38	5.61	0.816
	$n =$ 1.561	$n =$ 1.493	$n =$ 1.127	$n =$ 1.00	$n =$ 1.514	$n =$ 1.495	$n =$ 1.00

kinds of rubber was reversed. The viscosity of smoked sheet solutions had almost reached the level of the pure solvent, while the solution of pale crepe, which under the ordinary pressure of the viscosimeter showed a two-fold greater relative viscosity, still retained a certain structural measure (exponent $n = 1.127$). The solution curve of pale crepe, after the solution had been exposed for a month to the action of dispersed light, occupied approximately the same position as did the curve of a rubber solution milled hot for thirty minutes. The viscosity of the pale crepe solution dropped to the value of the pure solvent only after such a solution had been irradiated by rays of a mercury lamp in a quartz vessel for two hours. Such a difference between pale crepe and smoked sheet in respect to their aging in light is, it would seem, related to a darker coloration and consequently to a greater capacity for absorption by the smoked sheet.

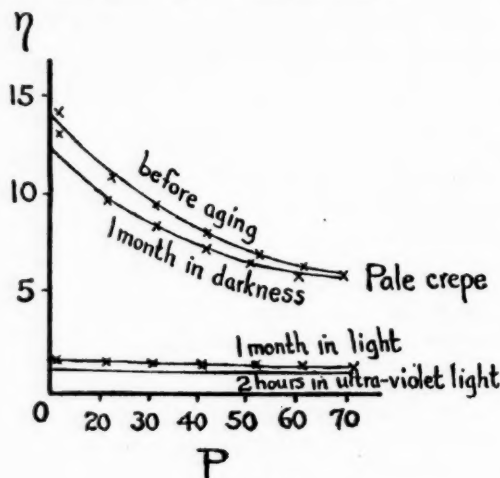


Figure 5

Our measurements of the structure viscosity of rubber solutions upon aging confirmed the suppositions expressed earlier by Bernstein¹⁴ and Garner,¹⁵ according to which aging in its first phase is a colloid-chemical process of disaggregation of the rubber micelles.

Results

1. Rubber solutions when flowing from a capillary tube at different pressures (in the Wilh. Ostwald viscosimeter with monostat of Wo. Ostwald) show deviations from the Hagen-Poiseuille law characteristic of colloids, and this agrees with the results of earlier investigators.
2. The dependence of the relative viscosity of rubber solutions upon the rate of flow or the pressure can be expressed by the de Waele-Ostwald formula: $\eta = KP^{1-n}$.
3. The exponent of the structure viscosity n in the de Waele-Ostwald formula can serve as a measure of the structure peculiarities of different types of rubber and characterize the aggregation processes which take place with the different changes in the rubber.
4. The viscosity of rubber solutions diminishes with increase in temperature, while the exponent of the structure viscosity increases.

5. During the milling of rubber, colloid-chemical processes of disaggregation of the rubber micelles take place, which are shown by a very great decrease in the structure viscosity exponents.

6. Similar processes occur during the aging of rubber solutions.

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- ² Wo. Ostwald, *Kolloid.-Z.*, **36**, 99, 248 (1925); **43**, 190 (1927); Wo. Ostwald and Auerbach, *Ibid.*, **41**, 56 (1927), etc.
- ³ Wo. Ostwald, *loc. cit.*
- ⁴ Kirchhof, *loc. cit.*
- ⁵ Wo. Ostwald, *Kolloid.-Z.*, **36**, 115, 248 (1925).
- ⁶ Herschel and Bulkley, *Kolloid.-Z.*, **39**, 291 (1926).
- ⁷ Kroeplin, *Kolloid.-Z.*, **47**, 294 (1929).
- ⁸ Haller and Trakas, *Kolloid.-Z.*, **47**, 304 (1929).
- ⁹ Wo. Ostwald, *Kolloid.-Z.*, **36**, 99 (1925).
- ¹⁰ Wo. Ostwald and Föhre, *Kolloid.-Z.*, **45**, 166 (1928).
- ¹¹ Nishikawa, *Kolloid.-Z.*, **38**, 328 (1926).
- ¹² Harries, *Kolloid.-Z.*, **33**, 181 (1923).
- ¹³ Kroeplin, *loc. cit.*
- ¹⁴ Fry and Porritt, *India Rubber J.*, **1928**, 131; *Trans. Inst. Rubber Industry*, III, 203.
- ¹⁵ Bernstein, *Kolloid.-Z.*, **12**, 193 (1913).
- ¹⁶ Garner, *Trans. Inst. Rubber Industry*, IV, 413 (1929).

The Surface Tension of Rubber Solutions

C. W. Shacklock

Introduction

During the past few years much attention has been paid to the constitution of raw rubber. The much improved methods of production of plantation rubber have resulted in a reasonably pure product available for investigation, and chemical analysis undoubtedly shows an empirical formula of C_5H_8 for the hydrocarbon. From this point onward, knowledge becomes less certain. Osmotic pressure and molecular weight measurements give no confirmation of a simple molecular structure, but show, in benzene solution, a behavior comparable with that of colloids. This is supported by experiments on swelling and viscosity, and by ultramicroscopic examination, all of which lead to the conclusion that rubber is a lyophilic colloid.

Hence arose the concept that the rubber particle is a polymer of simple molecules of formula C_5H_8 (possibly isoprene), such a structure being in agreement with the production of rubber-like substances by the action of sodium upon isoprene and butadiene (Harries, *Annalen*, 395, 211 (1912)).

The decrease in viscosity of a rubber solution with increasing periods of mastication of the rubber is hence regarded as a measure of depolymerization due to mechanical action; the increased ease of solution after mastication is confirmatory evidence.

Examination of substances other than rubber, *e. g.*, styrene and its products, indicates that most probably polymerization of simple molecules first takes place, followed by an aggregation of the polymers. Styrene will form at high temperatures, under the influence of hydrochloric acid, a polymer, distyrene, which has a definite boiling point and appears to be a chemical compound. Distyrene under the action of light produces a material resembling a jelly, of apparently very high molecular weight.

It is suggested (Auer, *Trans. Inst. Rubber Industry*, 4, 501 (1929)) that the styrene derivatives are two-phase systems, consisting of a higher polymer dispersed in a lower, and Auer extends this concept to raw rubber.

Pummerer (*Ber.* 60, 2148 (1927)) claims to have separated rubber into two phases, α and β rubbers, the former being soluble in ether. This is supported by Bary and Hauser. The two-phase structure of rubber forms a promising basis for the explanation of the interference diagrams produced when x-rays are passed through rubber under tension (Bary and Hauser, *Kautschuk*, 4, 96 (1928)).

On the other hand, Fikentscher and Mark (*Kautschuk*, 6, 2 (1930)) have suggested a spiral structure for the rubber particle requiring no two phases, which accounts completely for the x-ray diagrams. They explain the separation of the α and β rubbers of Pummerer by considering rubber to be a meshwork of long chains, from which ether, being a poor solvent for rubber, can dissolve a few of the less tangled particles. Benzene, however, being a good solvent, can completely disentangle the structure.

Stamberger (*J. Chem. Soc.*, 1929, 2318) has shown that solutions of various samples of rubber, including over-masticated rubber, up to a definite concentra-

tion give no change in vapor pressure, and hence concludes that rubber is of a very uniform nature and not a mixture of hydrocarbons of varying degrees of polymerization.

The heats of combustion of unmasticated and over-masticated rubbers have been measured by Messenger (*Trans. Inst. Rubber Industry*, 5, 71 (1929)), and shown to be the same within the limit of experimental error, the conclusion being that did depolymerization take place, these results should differ.

The suggestion that a type of "structure" persists in rubber, even when in solution, has been advanced by Klein and Stamberger (*Kolloid-Z.*, 35, 362 (1924)). Mastication is to be regarded as a breaking down of this structure, and Blow (*Trans. Inst. Rubber Industry*, 5, 417 (1930)) has shown that the viscosities of solutions of gas black mixings increase on standing, indicating the reappearance of structure.

Surface Tension

The surface tension of rubber solution has been measured as an attempt to draw some definite conclusion concerning the state of rubber when dissolved in benzene.

The extensive literature on surface tension measurements, both for pure liquids and for solutions, shows that such figures are easily and fairly accurately obtained. The presence of traces of impurities in a liquid are, generally speaking, indicated by a measurement of surface tension, and an application of the Gibbs absorption isotherm, while not accurate quantitatively, enables prediction to be made of the condition of a surface containing a solute adsorbed thereon from the bulk of the solution.

Few adsorption measurements have been attempted in organic solvents, but references are available to show that similar phenomena hold for such solvents as well as for water (Gilbert, *J. Phys. Chem.*, 31, 543 (1927); Holmes and McKelvey, *Ibid.*, 32, 1522 (1928)).

It should therefore be possible to detect depolymerization of rubber in, say, an over-masticated rubber by a comparison of the surface tension of solutions of equal strength of unmasticated and over-masticated rubber. Depolymerization will produce molecules differing widely in physical and chemical properties from the polymerized substance (*cf.* styrene and distyrene) and having most probably a different effect on the surface tension of the solution.

On the other hand, disaggregation of the dissolved substance in a solution is likely to produce no change in surface tension; aggregation implies merely coalescing of particles to form larger groups with no change in molecular species, and it is possible that in solution a dynamic equilibrium prevails between the particles and the aggregates, though the actual concentration of disaggregated material may be small.

Method of Measurement

Several methods are available for measurement of surface tension, and for solutions the following three are the simplest:

1. Drop method.
2. Capillary rise method.
3. Bubble pressure method.

Each method is capable of accurate measurement provided corrections are applied, but for rubber solutions it is obvious that the first two require modification to avoid errors due to solvent evaporation. Preliminary experiments showed

that considerable error is introduced in (1) when weighing the drop, and in (2) coagulation occurs in the capillary as the solvent evaporates. Only in the bubble pressure method can evaporation be successfully avoided in a simple manner.

The essential parts of the apparatus are identical with that used by Sugden as described by him in his book *The Parachor and Valency*. The modifications necessary for measuring rubber solutions are:

1. Oxygen, carbon dioxide, and water vapor must be removed from the air. Oxygen combines easily with raw rubber; water vapor appears to accumulate in the jet and cause fouling; and the effect of carbon dioxide is doubtful, but references are available to show that it is not altogether inert toward rubber (Pickles, *Trans. Inst. Rubber Industry*, 3, 66 (1927)).

2. The inert gas obtained as in (1) must be saturated with benzene vapor, otherwise rubber is deposited in the capillary due to evaporation of solvent.

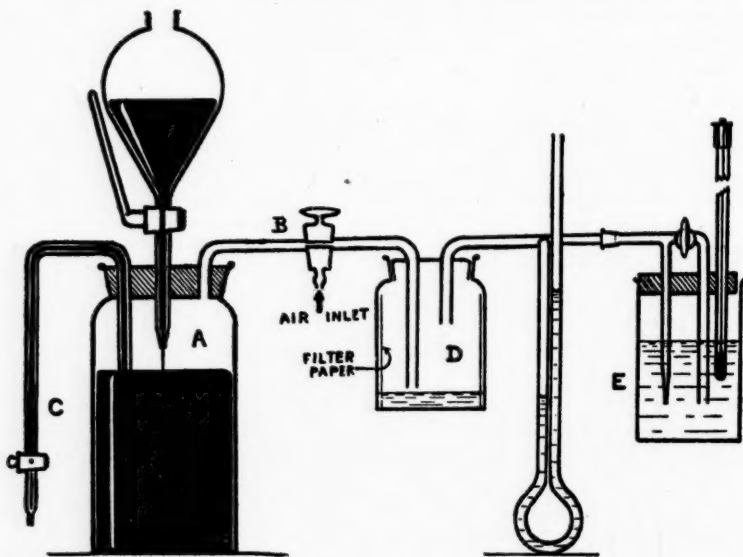


Figure 1

3. As manometric liquid, nitrobenzene was used since it was thought that alcohol, with a lower boiling point and hence higher vapor pressure, might by diffusion find its way into the solution under examination.

The apparatus is shown in Figure 1. The vessel A is first filled with dry mercury up to the three-way tap, B, which is in communication with a series of three potash bulbs. These contain potassium hydroxide solution, pyrogallol in potassium hydroxide and strong sulphuric acid, respectively, and serve to render atmospheric air suitable for the experiment.

On opening the syphon, C, "purified" air may be drawn through the potash bulbs slowly into A. When sufficient gas is obtained C is closed, the mercury transferred to the tap funnel, and B is turned to communicate with the rest of the apparatus. The latter consist of a small container with ground glass joint wherein the gas is saturated with benzene vapor, D, a manometer, and the capillary and wide bore tube as described by Sugden (*loc. cit.*). The vessel E, a weighing bottle

capacity 50 cc. in which the liquid to be examined was placed, is in a water bath of constant temperature (not shown in diagram).

It is necessary to sweep the apparatus with gas before the first experiment, and to have a very fine jet on the tap funnel to permit of very slow formation of bubbles.

The apparatus was checked before use by absolute measurements. These entailed a measurement of the radius of the capillary by a traveling microscope. The calibration of the latter was such that the error did not exceed 1 per cent, averaging six readings. The apparatus gave the surface tension of benzene as 28.6 and water 73.1 ergs per sq. cm. at 20.8° C. To obtain exact readings, benzene was taken as a standard. According to Sugden (*loc. cit.*) at constant temperature

$$\gamma = A P \phi$$

where γ = surface tension
 P = net gas pressure defined as:

the difference between the pressure required to liberate bubbles slowly from the capillary and the corresponding pressure for the wide bore tube. It is measured as

$$(H - h)gd \text{ where } \begin{aligned} H &= \text{manometer reading for capillary} \\ h &= \text{manometer reading for large bore tube} \\ d &= \text{density of benzene } (= 1.203 \text{ at } 20^\circ \text{ C.}) \\ A &= \text{constant for apparatus} \\ \phi &= \text{correction factor, given by} \\ &= 1 + 0.69 r \frac{gD}{P} \end{aligned}$$

$$\begin{aligned} \text{where } g &= 981 \text{ cm./sec.}^2 \\ D &= \text{density of liquid} \\ r &= \text{radius of larger tube.} \end{aligned}$$

Having measured r accurately as 0.124 ± 0.0002 cm., and taking γ for benzene as 28.80 (at 20.8° C., the temperature of experiment) ϕ is obtained as 1.0183, and A as 0.007047, and the surface tension of any solution is obtained simply by a measurement of P at 20.8° C.

Experimental

Measurements of surface tension were made on several rubber solutions, all at 20.8° C. It was possible to obtain consistent readings for all solutions which were not too viscous. For the purposes of comparison, all solutions were made at about 3 per cent. As far as surface tension measurements are concerned, the strength of the solution may vary slightly without sufficiently affecting the density to cause sensible error in the results, *e. g.*, taking the relative density of benzene at 20.8° C. as 0.876, and that of pale crepe as 0.931, the density of the solution becomes 0.878. This figure still holds for a 3.5 per cent rubber solution.

With highly viscous solutions the method breaks down since the liquid takes so long in re-forming across the mouth of the capillary that a continuous stream of bubbles is impossible.

The solutions were used as follows. All were kept in the dark until use. Twice distilled crystallizable benzene (b. p. 80–82° C.) was used in all cases.

(1) *Unmasticated Rubber*.—This solution took three weeks to form, and was stirred before using.

(2) *Partially Purified Pale Crepe Rubber*.—Pale crepe rubber was extracted with acetone for 6 hours, vacuum-dried at room temperature and dissolved in benzene. On solution, about two-thirds of the rubber was precipitated by alcohol,

this fraction being vacuum-dried as above and redissolved in benzene. Precipitation was repeated twice and the final product dissolved to produce a solution for measurement.

(3) *Cold-Masticated Rubber*.—The material was masticated on cold rolls for 2 hours. Solution appeared complete in 24 hours.

(4) *Hot-Masticated Rubber*.—The material was masticated for two hours on hot rolls ($T = 99^{\circ}\text{C.}$) and formed a homogeneous solution in 24 hours.

(5) Some of solution (1) was exposed to full radiation from a quartz lamp. The solution was in a quartz test tube, loosely stopped, and the light was focussed into the liquid by a quartz lens. A very rough comparison between the lamp and bright sunshine is to say that the effect of the former is between 100 and 200 times that of the latter. Eight hours reduced a highly viscous liquid to a liquid almost as mobile as benzene.

(6) *Air-Heated Rubber*.—Pale crepe rubber was heated in an air oven with free air circulation for 10 hours at $155\text{--}160^{\circ}\text{C.}$, and then placed in benzene. Solution occurred in 2 days.

(7) *Vacuum-Heated Rubber*.—Pale crepe rubber was placed in a tube and the latter exhausted on a water pump. During this time the tube was heated in boiling water to drive off moisture. With the apparent removal of the moisture the process was repeated on a "Hyvac" pump, exhausting to 0.01 mm. mercury. The tube was then sealed and heated in the same oven as specimen (6). The resulting solution took about 10 days to become homogeneous, and though of the same strength as (6) was much more viscous.

Results

The following are the results obtained as an average of three readings on each solution. Agreement between the individual readings was very good, and the error on the results below may be taken as within 0.1 unit.

$T = 20.8^{\circ}\text{C.}$

Pure benzene (standard).....	28.80 ergs per sq. cm.
1. Unmasticated rubber.....	28.86 ergs per sq. cm.
With this solution several dilutions were used, and in all cases agreement was found well within the limit of error, the result given above being an average.	
2. Partially purified rubber.....	28.86 ergs per sq. cm.
3. Cold-masticated rubber.....	30.74 ergs per sq. cm.
4. Hot-masticated rubber.....	29.34 ergs per sq. cm.
5. Rubber exposed to U. V. radiation.....	28.51 ergs per sq. cm.
6. Air-heated rubber.....	28.91 ergs per sq. cm.
7. Vacuum-heated rubber.....	28.98 ergs per sq. cm.

Discussion of Results

The following points are to be noted:

1. The surface tension of rubber is neither affected by resins nor does an approximate fractional precipitation produce a product at variance with the original material. (Exact agreement between the first two results is accidental.) It may be assumed that in Results 3, 4, 5, and 6, a considerable lowering of viscosity takes place due to the treatment the rubber has received. This was observed but not measured as the facts are commonly known. With regard to Results 6 and 7, Fry and Porritt (*Trans. Inst. Rubber Industry*, 3, 203 (1927)) showed that oxygen absorbed by rubber before solution lowers the viscosity of the resulting solution.

2. The absorption of oxygen as shown by Fry and Porritt (*loc. cit.*) has no effect on the surface tension within experimental error.

3. In an investigation to be published at a later date, Cotton has shown that rubber worked in an internal mixer for one hour in the cold and in total absence of oxygen shows practically no sign of mastication.

4. Mastication on open rolls (Results 3 and 4) produce solutions of different surface tension from the remaining solutions. The effect is greater where more power is used, *i. e.*, on cold rolls.

The lowering of viscosity in a rubber solution may be brought about in several ways, and is commonly attributed to disaggregation. This is supported by the surface tension measurements in Results 5 and 6, where no appreciable change takes place. If depolymerization occurred in both solutions some change in surface tension should have been observable. The slight but definite lowering of surface tension brought about by the action of ultra-violet light is possibly due to depolymerization by the radiation. This point requires further investigation.

With regard to Results 6 and 7, it may be seen that the absorption of oxygen due to heating rubber in air, gives a product which forms a solution, having a surface tension not differing from that of a solution of untreated rubber. Hence neither disaggregation solely, nor oxygen absorption solely, affects surface tension. When, however, these two effects are combined in mastication on open rolls, an effect is noticed which is greater when less heat is present.

It therefore appears that for mastication to be produced, two factors are involved: (a) mechanical action such as is obtained in mixing machinery; (b) absorption of oxygen. Neither of these effects separately will produce a masticated rubber.

This conclusion is supported by Daynes (*Trans. Inst. Rubber Industry*, 3, 437 (1928)) who states that the absorption of common gases by rubber decreases with rise of temperature, and is a volume and not a surface effect. (There is obviously a close analogy between absorption and solution.) Mastication is more pronounced when the rubber is worked cold, and as the absorption of atmospheric oxygen is greater the lower the temperature, this latter may account for the difference in the surface tension of solutions of cold and hot masticated rubbers. It must be noted that the absorption of oxygen by air-heated rubber (Results 6 and 7) has no effect on the surface tension of the resulting solution. At the same time disaggregation occurs, as indicated by rapid solution and a lowering of viscosity.

One point as yet unexplained is the rise in surface tension of solutions produced by cold and hot masticated rubber. These figures must be in agreement with the fact that no change in surface tension occurs by air-heating the rubber, when both disaggregation and slight oxygen absorption takes place.

The author suggests the following explanation. The rise in surface tension is due to a compound formed between oxygen and disaggregated rubber. This compound is not formed unless milling accompanies the oxygen absorption and is most probably due to the oxygen being converted to ozone by electrical effects on the rolls. This is supported by the well-known fact that ozone attacks rubber. Without electrical effects the oxygen merely stays in solution in the rubber and the effect of a gas dissolved in a lyophilic colloid on the surface tension is most probably very small (Freundlich, *Colloid and Capillary Chemistry*, English translation of 2nd German edition, p. 366).

Mechanical treatment, ultra-violet light, heating in oxygen or in air, all produce disaggregation in raw rubber. Hence, if it were possible to eliminate electrical effects in mastication, little change should take place in the rubber. This occurs when raw rubber is being washed. The rubber is worked on cold rolls, but the accumulation of a static charge is impossible owing to the washing water. This suggests an explanation of the non-mastication of rubber when being washed.

A final point appears highly significant. The surface tension of many of the solutions examined does not differ from that of pure benzene within experimental error. This offers support to the statements of Stamberger and Blow (*Nature*, 13, 124 (1929)) wherein the "structure" of rubber is shown from vapor pressure measurements to persist even in dilute solution, and also with masticated rubber. Did such a structure exist, the rubber might not approach the surface closely enough to influence surface forces. Any measurement on such a solution will therefore be a measurement of the surface tension of the pure solvent.

Further work is indicated, particularly on concurrent measurements of surface tension, viscosity, oxygen absorption, and the elimination of electrical effects in mastication.

Technical Note on the Use of Certain Solvents in Solutions

H. Coulangeon

A general procedure for making two pieces of vulcanized rubber adhere consists of putting between them a thin layer of fresh, tacky rubber obtained from a solution of pure rubber in a solvent (such as benzene, toluene, etc.). The two surfaces to be joined are first cleaned, or even scraped, and coated with the solution.

After suitable drying, the two surfaces are pressed firmly together for some minutes, or they are struck many times with the hammer and anvil so as to be certain of close contact. If the operations have been correctly carried out and the solution is of good quality, that is, prepared by a standard procedure and first tested in the laboratory, the adherence will usually be good. But it may happen to be poor or even very bad for the following reason:

The volatile solvent brings about by its evaporation a very considerable local drop in the temperature; the layer of air with which it is in contact becomes cooled, and if the hygrometric state is raised its water vapor settles out (dew point). The quantity of this vapor is more or less great and the waste more or less serious.

We shall discuss these various points and give rules which can be followed to suit the particular conditions involved.

Let us consider the following four solvents:

	Density
A—Solvent naphtha	0.860
B—Toluene	0.870
C—Aviation gasoline	0.710
D—Benzene	0.800

which will be used in preparing four test solutions of approximately the same viscosity. The lowering of the temperature of a surface coated with each one of these will be determined.

To do this, a thermometer is inserted in the solution to just above the bulb, withdrawn and suspended in the enclosed space at the temperature at which the experiment is carried out, where it will oscillate slowly and almost constantly.

The minimum temperature obtained is read directly, and this corresponds to the surrounding temperature and to that of the solution used (A, B, C, D), which is also assumed to be the temperature of the interior. The temperature lowerings are deduced from this. This is done for each of the solutions. The results are shown in Fig. 1.

The measurements were made between 10° and 30°, which appeared to be the extremes of temperature in industrial operations.

Figure 2 gives directly the minima temperatures recorded above (Curves A, B, C, D), and also the dew points for the various values (shown on the oblique lines) of the hygrometric state as a function of the surrounding temperature.

If F is the maximum vapor pressure of water at temperature t of the surrounding air, and f its actual vapor pressure, the hygrometric state $e = 100 F/f$. At $e = 100$ ($f = F$) the air is saturated, there is condensation, and it is the dew point.

If this is so, each of the Curves A', B', C', and D', divides that portion of the diagram which interests us into two sections.

1. For all points in the upper region and for all points of the curve in question, there is condensation on the cemented portion of the samples, and a good adherence is impossible.

2. For all points of the lower region, condensation cannot take place, therefore good adherence is possible.

Let us suppose that we are using a benzene solution, and take a point, M , located on the diagram above Curve D' , of which the coordinates are: hygrometric state 50, temperature 24° .

The corresponding dew point is 12° , therefore the temperature of the cemented surface drops to 10° , and condensation takes place. In order that there shall be good adhesion, heating is necessary.

In fact for a limited atmosphere not containing any supply of water, the hygrometric state decreases with increase of temperature (F increases).

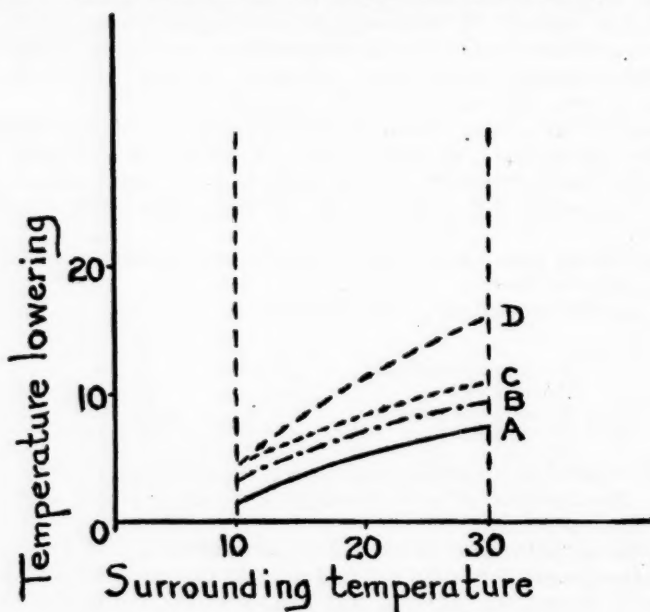


Figure 1

Figure 3 shows some typical curves representing these variations for different initial values of the hygrometric state. Upon heating, therefore, point M is displaced parallel to the X axis (Fig. 2) and on the corresponding curve of the hygrometric variable (Fig. 3). It meets at M' , Curve D' (Fig. 2). At this point ($e = 40.5$; $t = 27^\circ$), there is still condensation.

Continuing the heating, one reaches the lower region of Curve D' , where there is no longer condensation.

It is seen then that with the solution used and the hygrometric state given, it will be necessary to heat the medium to at least 27° to avoid condensation. This temperature is too high for a factory where, for the comfort of the workers and for a good output of hand labor, the temperature should not be above 25° .

Still, the case under consideration is relatively favorable. Considering now point M_1 ($e = 70$; $t = 22^\circ$), which is frequently the case in summer and may be

encountered in spring and autumn, it is seen that it will be necessary to heat to at least 33° if benzene is used.

It would therefore be better to change the solvents and have recourse to toluene or aviation gasoline, which require heating to 27° and 25° , respectively. If the conditions are even more unfavorable, and correspond for example to M_2 ($e = 80$; $t = 26^{\circ}$) (certain cloudy days), it will be necessary to use solvent naphtha.

It should be understood that the procedure depends on the type of manufacture and its extent.

It is difficult and at times practically impossible to have ready for use at the same time several different solutions; therefore in general it would be better to select a solvent for summer and one for winter use.

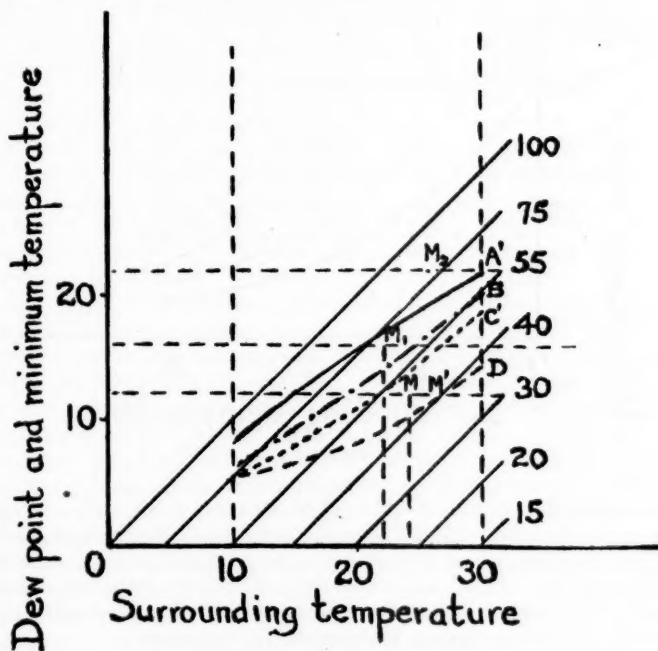


Figure 2

It is a problem for each one to perfect for himself, according to the possibilities and requirements of his factory. Several thermometers are sufficient for all the measurements, two of which are used in psychrometry, a condensation hygrometer being almost a luxury.

All these remarks apply to cold vulcanization of certain cements.

The cooling of the cemented portion (previously dried in a hot chamber) is brought about just after wetting in a solution of sulfur chloride solvent. The difficulty here cannot be remedied because the coated parts must be immediately joined and struck. Accordingly they have not time to take up the temperature of the surrounding medium, and the deposited water vapor, if any is present, is confined in the joint which is inevitably bad and cannot be done over. The phenomenon of cooling described above is evidently general and is produced with all solutions, whether loaded or not.

However, it is not very well defined and has only disastrous results with solutions of pure rubber and solvent, which are the only solutions used for cements described above, where one must join the coated parts after only a few minutes' drying, the pieces themselves being already vulcanized.

As described above, in cementing pieces which are to be vulcanized later, pure solutions are used. In this case, the pieces are usually heated in an oven, before curing, for twenty-four or forty-eight hours. Care must be taken to have the temperature of the oven high enough to drive off the water deposited. This is not always possible, for other reasons, if the quantity of water is very great.

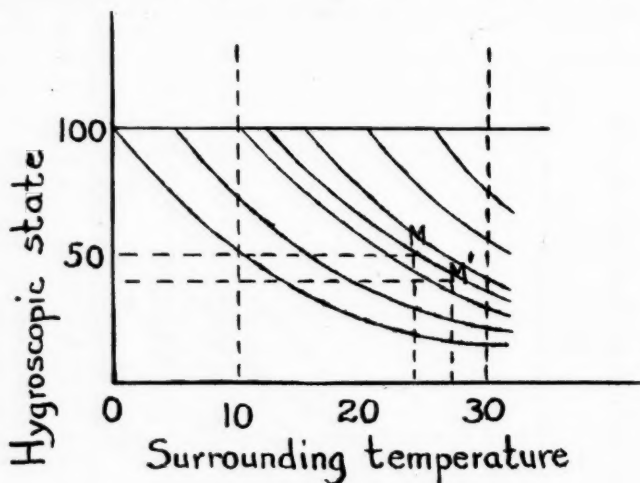


Figure 3

All these precautions are not sufficient to secure a good bond.* Great care in manufacture must still be taken over and above this. We have pointed out this inconvenience because it is a very frequent cause of waste, often escaping attention. All rubber technicians know how difficult it is to define the conditions for good manufacture, and how easy it is to pass from good to poor and to bad when apparently the processes have not changed.

Isoprene and Rubber

XXIV.¹ The Reduction of Rubber with Hydriodic Acid

H. Staudinger and James R. Senior²

EDG. TECHNISCHE HOCHSCHULE, ZÜRICH

In the past, the reduction of rubber has been of special interest since Harries³ was of the opinion, based on his ideas on the constitution of rubber, that hydorrubber might possibly be distilled without decomposition *in vacuo*, and therefore that its preparation would be of importance in explaining the constitution of rubber.

Staudinger and Fritsch⁴ obtained a hydorrubber by catalytic reduction, which they considered to be a high molecular paraffin hydrocarbon; in the distillation it cracked and yielded low molecular cleavage products. It was concluded from this that rubber must also be a high molecular hydrocarbon. Contrary to this opinion, there was the evidence that the hydorrubber had the same appearance as rubber and dissolved readily in solvents like ether, and therefore showed essential differences from high molecular paraffins of known constitution as, for example, dimyricyl. Since hydorrubber has a branched chain, it might be thought that it differed from dimyricyl on this account.

It was surprising, however, that in the reduction of butadiene rubber the hydrogenation product⁵ obtained likewise does not possess the physical properties of a high molecular paraffin hydrocarbon, although here properties similar to those of high molecular paraffins are to be expected, since a normal paraffin chain should result from the reduction of butadiene rubber. These problems were sufficient inducement for preparing⁶ hydorrubber in still another way. Berthelot⁷ had already many years ago converted rubber with hydriodic acid at an elevated temperature into paraffin hydrocarbons, which distilled above 350° without decomposition. One might assume, therefore, that there is perhaps in this substance the true hydrogenation product of rubber which was sought by Harries, whereas in catalytic hydrogenation the rubber micelle assumed by Harries is not completely split up.⁸

Such was the situation a few years ago, and it is of interest even now in explaining the constitution of rubber⁹ to call attention to the original difficulties in obtaining a simple picture of the constitution of rubber from all the experimental facts.

In repeating Berthelot's experiment, we obtained a saturated hydrocarbon of waxy appearance, therefore a product which is more like a paraffin in appearance than the hydorrubber obtained by reduction. The hydrocarbon is stable to bromine and concentrated nitric acid, like hydorrubber. Unlike Berthelot's results, our product could not be distilled without decomposition, but it decomposed with formation of volatile products and a considerable residue. Analysis showed that it contained about 1% more carbon and 1% less hydrogen than is to be expected in the case of a high molecular paraffin, whereas hydorrubber gave analytical values corresponding to C_5H_{10} . The average molecular weight of the hydrocarbon is 1200, if the reduction is carried out at 280°; on the contrary it amounts to 1700 if it is prepared at 250°. There the products formed are not identical, but there is a lower molecular hydrocarbon formed at the higher temperature than at the lower.¹⁰

Meanwhile the work of Widmer and Geiger has proved that the eucolloidal rubber can easily be converted into hemicolloidal cyclorubbers.¹¹ It is known further that the rubber molecule is very sensitive, is easily cracked by heating, and the higher

the temperature of cracking the smaller are the molecules formed in the decomposition.¹² Finally it is known from studies on viscosity that the rubber molecule is easily split up by strong acids, like hydrogen halides.¹³

Likewise the action of hydriodic acid on rubber at higher temperature is easy to understand. Upon heating with hydriodic acid, there first occurs a decomposition of the rubber molecule, and the higher the temperature at which the reaction is carried out the smaller are the fragments. These fragments are partially cyclized by the action of the acid, and in this way the double bonds are broken up. The cyclo product is then reduced. Therefore the reduction product has a higher carbon and smaller hydrogen content than that calculated for $(C_5H_{10})_x$. Like hydorrubber, it also has a somewhat different appearance from hydrocyclo rubber.¹⁴ The viscosity of its solution is very small compared to that of rubber, and this is understandable in the light of recent experiments on hemicolloids.¹⁵

The hydrocarbon of Berthelot is accordingly not a high molecular paraffin, but a hemicolloidal hydrogenation product of a cyclorubber. This reduction does not permit any conclusions on the constitution of rubber.¹⁶

Experimental Part

Reduction of Rubber with Hydriodic Acid.—The experiments were carried out in accordance with directions given by Berthelot. Three grams of extracted rubber were heated with 30 g. of concentrated hydriodic acid (sp. grav. 1.96) with the addition of 1.5 g. of red phosphorus in one experiment for 24 hours at 245–250°, and in another experiment for 24 hours at 280°. Completely saturated hydrocarbons were formed. At a lower temperature, 200°, the reduction was not complete. In most cases at higher temperatures, the tube broke. On completion it was taken up in benzene, filtered and agitated with soda solution, and with sodium thiosulfate to remove iodine. By deposition of the concentrated benzene solution, the products were obtained first as greasy masses, and after repeated reprecipitations as waxy masses. The hydrocarbons are readily soluble in benzene and chloroform, insoluble in alcohol and acetone, and are therefore similar in their solubility to rubber and cyclorubber. The solutions have very low viscosities, since they comprise hemicolloidal decomposition products.¹⁷ The reduction products are saturated to bromine solution, stable to oxidizing agents like concentrated nitric acid and therefore behave like hydorrubber and like high molecular paraffins.

ANALYSIS OF PRODUCTS PREPARED AT 280°

0.1334 g. substance yielded 0.4224 g. CO_2 and 0.1584 g. H_2O

0.0162 g. substance, 0.2920 g. camphor, $\Delta = 1.82^\circ$

$(C_5H_{10})_x$	Calculated:	C 85.71	H 14.28%	Molecular weight	—
	Found:	C 86.36	H 13.29%	Molecular weight	1220

ANALYSIS OF PRODUCTS PREPARED AT 250°

0.1174 g. substance yielded 0.3724 g. CO_2 and 0.1404 g. H_2O

0.015 g. substance 0.2962 g. camphor $\Delta = 1.15^\circ$

$(C_5H_{10})_x$	Calculated:	C 85.72	H 14.28%	Molecular weight	—
	Found:	C 86.52	H 13.38%	Molecular weight	1760

References

- ¹ Part XXIII, *Ber.*, **63**, 2900 (1930).
- ² This work was carried out in 1923.
- ³ Harries, *Untersuchungen über die natürlichen und künstlichen Kautschukarten*, page 48.
- ⁴ Staudinger and Fritsch, *Helvetica Chim. Acta*, **5**, 785 (1922).
- ⁵ Staudinger, *Ber.*, **57**, 1203 (1924); *Theses*, E. Geiger and E. Huber, Zürich, 1926.
- ⁶ Staudinger and Widmer, *Helvetica Chim. Acta*, **9**, 529 (1926).
- ⁷ Berthelot, *Bl.*, [2] **10**, 436 (1868); *Ibid.*, [2] **11**, 53 (1869).

⁸ This might be compared with the concepts at the time on the constitution of rubber. Kirchhof, *Kolloid-Z.*, **14**, 38 (1914).

⁹ See Part XXI, *Kautschuk*, **1930**, 154.

¹⁰ For the decomposition of rubber at different temperatures, see Staudinger and Bondy, *Ann.*, **468**, 1 (1929).

¹¹ Parts 9 and 10, *Helvetica Chim. Acta*, **9**, 549 (1926).

¹² Staudinger and Geiger, *Helvetica Chim. Acta*, **9**, 549 (1926); Staudinger and Bondy, *Ann.*, **468**, 1 (1929).

¹³ *Ann.*, **468**, 13 (1929); and *Ber.*, **63**, 2888 (1930).

¹⁴ For powdered hydrocyclorubber, see Staudinger and Widmer, *Helvetica Chim. Acta*, **9**, 544 (1926); *Thesis*, E. Geiger, Zürich, 1926.

¹⁵ Staudinger, *Ber.*, **59**, 3031 (1926); *Kolloid-Z.*, **51**, 71 (1930).

¹⁶ Also see Pickles, *J. Chem. Soc.*, **97**, 1085 (1910) and remarks by Harries, *Ann.*, **383**, 227 (1911).

¹⁷ Unfortunately the viscosity of the preparations at the different temperatures was not compared, since at the time that the experiments were carried out (1923) the significance of investigations of viscosity in the explanation of the constitution of high molecular compounds was still not realized. The product prepared at 240° would have to give a solution of somewhat higher viscosity than that prepared at 280° would give.

Isoprene and Rubber

Part 32.¹ The Constitution of Rubber

H. Staudinger

FREIBURG, I. B.

PART I

Pummerer² has recently published in this journal an article on the constitution of rubber which repeats his address before the general meeting of the Colloid Society. In it he describes his efforts to obtain a new insight into the molecular magnitude of rubber by the discovery of special groups, namely, end groups, within the molecule. This work has already contributed largely toward an understanding of the constitution of high polymeric substances, and therefore the attempt is being made with the material at our disposal to decide whether this is of use in explaining the constitution of rubber.

1. End Groups in the Polyoxymethylenes

When about ten years ago the problem of the constitution of high polymeric substances was first attacked by my collaborators and myself, a special effort was made to determine the unknown and by ordinary methods indeterminable molecular weight of this insoluble or colloiddally soluble compound by means of an indirect method. The older view of the constitution of high polymeric substances assumed that in these high polymers numerous individual molecules were united in long chains, though it had been possible to obtain no data on whether the degree of polymerization of high molecular substances is 10, 100, or 1000.

As a beginning, the determination of the problematical molecular weight of the insoluble polyoxymethylenes had been successful, and the method of determining the end groups had played an important part in this work. An homologous polymeric series of polyoxymethylene diacetates was prepared by acetolytic cleavage. It was possible to prove with the soluble members of this product that the molecular weight, obtained by finding the acetyl content, agreed with that determined by the cryoscopic method. At the same time it was proved that the acetyl was located in characteristic end groups in the molecule, and not in acetic acid which had been adsorbed³ by one of the simple polymeric substances⁴ in quantities which depended upon their degree of dispersion in solution. On the basis of this proof, it could be concluded that in corresponding insoluble polyoxymethylenes which represent the end members of the series of high molecular polyoxymethylenediacetates, acetic acid is combined at the end of the long chains. Therefore it was possible to estimate the molecular weight from the acetic acid content of this product, which could not be done by other methods. In these substances at least fifty individual molecules are united in a long chain.⁵

In addition, an homologous polymeric series of polyoxymethylenedimethylethers was prepared. With the lower members the molecular weight obtained by analytical determination of the end groups agreed with that determined cryoscopically. The highest molecular dimethylether is α -polyoxymethylene,⁶ which in its chemical properties agrees perfectly with the lower members, but is distinguished from the latter by its insolubility. A degree of polymerization of about 100 was found for this insoluble product by a determination of the end groups.

Thus the existence of the long molecule which had previously been conjectured was proved by experiment for the first time. On the basis of this result, an analogous structural principle was assumed for other high molecular natural substances like cellulose. In this way it happened that a number of investigators again gave consideration to the old ideas, after other views had been proposed as a result of x-ray investigations.⁷

It is much more difficult to explain the constitution of α - and β -polyoxymethylene,⁸ because here a series of homologous polymeric products from the lowest to the highest molecular weight is lacking. β -Polyoxymethylene often contains a small quantity of sulfuric acid, and produces a sulfuric acid ester of polyoxymethylenedihydrate. However, from this sulfuric acid content, which is assumed to be an end group of the molecule, one is not justified in coming to a conclusion in regard to the size of the molecule, because it would have to be proved that the complete β -polyoxymethylene has a homogeneous polymeric structure, and therefore consists only of molecules of this polyoxymethylene sulfuric acid ester. This cannot be proved, and therefore the sulfur content cannot be utilized to estimate the average molecular weight.

To mention a further example, it is likewise not possible to calculate a molecular weight for starch from the phosphoric acid content of amylopectin,⁹ because it is not known whether this is a homogeneous product of the phosphoric acid esters of a polymeric maltose anhydride.

Therefore the determination of the end group does not always permit a judgment of the size of the molecule. This method is applicable if a polymerically homogeneous substance is concerned. Estimates can be made only if it is possible to prepare a homologous polymeric series of compounds, and to study the properties of the corresponding compounds of the lower members.¹⁰ Only in a few cases therefore was it possible to obtain information on the structure of the large molecules of a high molecular compound in the sense of the Kékulé structure. On the basis of the physical properties of colloiddally soluble compounds, particularly through viscosity measurements, it is possible today to establish the magnitude of the molecule.¹¹ However, the end groups of the long molecules which do not govern the physical properties, and yet do influence the chemical reactions,¹² are for the most part unknown.

2. End Groups of Hemi-colloidal Hydrocarbons

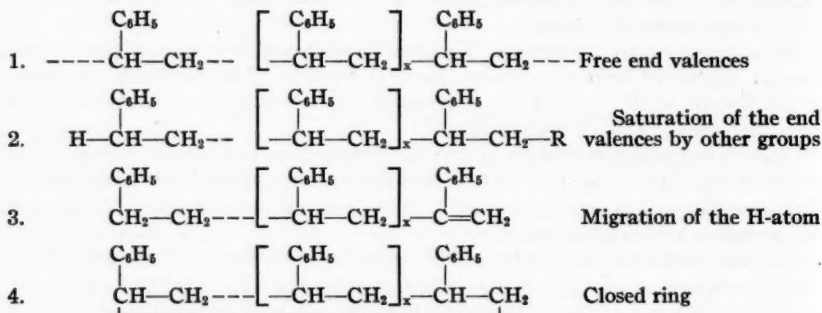
Hemi-colloidal hydrocarbons, *i. e.*, products having molecular weights of 1000-10,000, were studied, particularly in the series of polysterols and polyindenes, because these are especially stable. The molecular weight of these compounds could be determined cryoscopically, since in the case of these relatively small molecules the molecular weight is determined within a range of concentration in which the molecules still move freely.¹³ In this case the important fact was proved that the molecules can be subjected unchanged to chemical reactions, and that they therefore must be constituted like other molecules. Thus in the conversion of polysterols¹⁴ and polyindenes¹⁵ into the corresponding hexahydro products, the average molecular weight does not change.

For a complete explanation of the constitution, *i. e.*, a complete understanding of the structure of the polymeric molecule, not only is a knowledge of the molecular weight necessary, but one must know also how the molecule is constructed. In an address at Düsseldorf¹⁶ the following was said in this connection:

"After it has thus been established that the polymerization of unsaturated compounds takes place through normal valences, the second and more difficultly answerable question arises, how is the molecule defined? In a symmetrical ar-

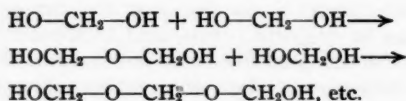
rangement of 20-100 sterol molecules, free valences could be present at the ends (Formula 1). This is certainly not the case because the 3-valence hydrocarbon atom on the end of such a chain cannot be easily detected. It was supposed in the beginning that as in the case of polyoxymethylenes the free end valences were replaced by another group, for example, by HCl, in case of the formation of hemi-colloids, with tin, or tetrachloride as catalyst (Formula 2).

"Brunner and Ashdown were able, however, to prove definitely that this is not true of polyindene and polysterol. Further there is the possibility that the process of polymerization results from the usual addition of one molecule to a second, with migration of an atom of hydrogen. The molecules must then have a double bond at the end (Formula 3), which cannot be proved for polysterol. Naturally the experimental difficulties in distinguishing a single double bond are extraordinarily great in a hydrocarbon of a molecular weight of about 3000. However, the end valences themselves might be saturated in a closed ring. In these polymers there appear mixtures of from 40- to 200-membered rings¹⁷ (Formula 4)."



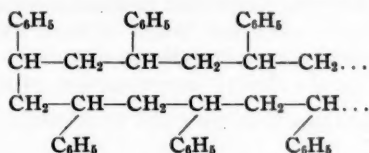
In a later work this question is dealt with in more detail.¹⁸ More accurate experimental investigations of the constitution of polyindenes and polysterols indicated that in this case it is very probable that high molecular rings are present. In this case characteristic end groups cannot be detected, in distinction to the case of polyoxymethylenes.

The difference in structure of high molecular hydrocarbons and polyoxymethylenes depends upon a fundamental difference in the process of polymerization. The polyoxymethylene chains are formed by condensation polymerization,¹⁹ a molecule of formaldehydehydrate with cleavage of one molecule of H₂O, according to the following formula:



The polysterols originate, on the other hand, through true polymerization processes. Here numerous other molecules are added on to an active molecule of monomeric sterol, until finally the free end valences are saturated with formation of a closed ring. According to previous experiments, the size of the molecule depends upon the rate of polymerization. In the case of rapid polymerization, for example, in the polymerization of sterol by heat or with catalysts, polysterols of

a hemi-colloidal character are formed, while at lower temperatures or without catalysts very high molecular eucolloidal products are formed.²⁰



3. End Groups in Rubber

On the basis of these results with synthetic high polymers, one can judge whether it is possible to determine from the end groups the molecular weight of rubber, which cannot be determined by cryoscopic measurements, and accordingly whether by the aid of this method an exact determination of the constitution of rubber can be made. Such a procedure gives promise of success if a homologous polymeric series of compounds of similar structure is concerned, where in its lower members it is proved that the molecular weight, determined by the cryoscopic method, agrees with that determined by the end group method, and further that the "foreign group" is really an end group. In this way Bergmann and Machemer²¹ have attempted to determine the molecular weight of cellulose decomposition products.²² However, such homologous polymeric series of compounds with characteristic end groups are not known in rubber. Such products can be obtained by the decomposition of rubber by bromine or oxidizing agents, but this procedure offers little prospect on account of the complicated structure and the great reactive capacity of the rubber molecule.²³

Rubber has an extraordinarily high molecular weight, and here arises a further difficulty in determining the molecular weight by the aid of end groups. In compounds having a molecular weight above 10,000, one end group forms only a very small part of the molecule, less than 1%. Analytical errors, therefore, play a great part.

In the rubber hydrocarbon the end group can be only a hydrocarbon residue, therefore a very similar group, and this makes the determination still more difficult.

As a result of these difficulties there is no evidence that the end group method of determination, which in a few cases leads to valuable results, can furnish essentially new contributions to an explanation of the constitution of rubber.

PART II

1. The Determination of the Molecular Weight of Rubber

The molecular weight of rubber is obtained in a manner wholly like that of the macromolecular polysterols, of which the determination has been calculated in an earlier communication in this Journal.²⁴ The molecular weight of hemi-colloidal polysterols can be determined cryoscopically. There is in this instance a relation between the molecular weights and the viscosities of solutions of the same concentration of different homologous polymeric compounds.²⁵

This relation is an extremely simple one: the specific viscosity of solutions of the same concentration increases in proportion to the length of the fiber molecule. This law is explained by the fact that the interference in the stream of liquid increases not only proportional to the mass of dissolved substances, as the Einstein law requires, but further it changes in proportion to the length of the molecule

at constant concentration. This simple law allows only a conclusion as to the molecular size of the macromolecular polyesterols, whose molecular weight cannot be determined directly, with the result that in these eucolloid products there are organic compounds having a molecular weight of from 100,000 to 200,000.

With derivatives of rubber, the relations between viscosity and molecular weight are determined²⁶ from hemi-colloidal decomposition products. The constant

$$K_m = \frac{\eta_{sp}}{cM} \text{ here has the value } 3 \times 10^{-4}.$$

It is surprising that the constant K_m also has the same order of magnitude²⁷ in hemi-colloidal hydorrubber. This is an indication that the viscosity of homopolar solutions of hydrocarbons is really due to the length of their molecules and that the differences in the structure itself, which are chemically very pronounced, are of secondary influence.

Based on viscosity measurements of solutions of rubber which have not been broken down, rubber has molecules with a molecular weight of 50,000 to 200,000.

TABLE I

Substance	Molecular Weight in Benzene	Relative Viscosity $\eta_r = \eta_c / \eta_L$ of a 0.25 mol. C_6H_6 Solution	Specific Viscosity $\eta_{sp} = (\eta_r - 1)$	$\frac{\eta_{sp}}{c}$	$K_m = \frac{\eta_{sp}}{cM} \times 10^{-4}$
Rubber decomposed in tetralin.....	3400	1.263	0.263	1.052	3.1×10^{-4}
Rubber decomposed in xylene.....	4250	1.285	0.285	1.140	2.7×10^{-4}
Gutta-percha decomposed in tetralin	6400	1.507	0.507	2.028	3.2×10^{-4}
Gutta-percha decomposed in xylene.	2700	1.200	0.200	0.800	3.0×10^{-4}

TABLE II

Product	Molecular Weight in Benzene	$\frac{\eta_{sp}}{c}$	K_m
Hydorrubber.....	4550	1.2	2.6×10^{-4}
Hydrogutta-percha.....	5360	1.64	3.0×10^{-4}
Hydorrubber.....	2700	0.92	3.4×10^{-4}
Hydorrubber.....	1600	0.48	3.0×10^{-4}

TABLE III

Substance	Molarity	η_{sp}	$\frac{\eta_{sp}}{c}$	$M = \frac{\eta_{sp}}{c K_m}$ $K_m = 3 \times 10^{-4}$	$M = K_c \times 10^4$ (Note 28)	Degree of Polymerization
Raw <i>Hevea</i> rubber.....	0.0125	0.68	54.4	180,000	160,000	ca. 2500
Rubber purified according to the method of Pummerer						
Difficultly soluble.....	0.025	0.543	21.8	73,000	77,000	ca. 1000
Easily soluble.....	0.025	0.389	15.5	52,000	56,000	ca. 800
Balata.....	0.025	0.386	15.4	52,000	51,000	ca. 750
Masticated rubber.....	0.025	0.19	7.6	25,000	30,000	ca. 400

In the rubber macromolecules there are accordingly at least 1000 isoprene residues united to one long fiber molecule. The position of the end valences of the long chains is uncertain.²⁹

The order of magnitude of the molecular weight undergoes no essential fundamental changes in the more exact determination of constant K_m . A molecular weight of rubber as high as about 5000, as assumed by Meyer and Mark,³⁰ and again by Pummerer,³¹ should no longer be considered, on the basis of this investigation.³² Many hydrocarbons are known of a molecular weight of about 5000,

such as the hemi-colloidal decomposition products of rubber, the hemi-colloidal polyesterols and polyindenes which have properties wholly different from rubber, as has already been known for many years. A comparison of these hemi-colloidal products with rubber shows that the latter is quite differently constituted, namely, that it must have a much higher molecular weight than the hemi-colloidal hydrocarbons.

2. The Nature of the Colloidal Solution of Rubber

The structure of rubber from macromolecules explains both its physical properties, *i. e.*, the remarkable viscosity of its solution and also its great reactivity. The special viscosity of rubber solutions depends upon the fact that the sphere of action of the macromolecules is very great. In solutions of the same concentration of polyrenes of different average molecular weight, the number of molecules decreases proportionately to the average molecular weight, but the sphere of action increases with the square of the length of the molecules. Therefore the dissolved molecules of high molecular rubber in 1-2% solution have such a great sphere of action that it is greater than the volume concerned. Such a solution no longer represents a normal solution or sol solution in which the molecules move freely, but it is a gel solution.³³ In such a case abnormal viscosity results from the mutual disturbance of the long molecules. The viscosity no longer increases proportionately to the increase in concentration, but much more rapidly, since the mutual interference of the long molecules becomes constantly greater with increasing concentration. Furthermore, deviations from the Hagen-Poiseuille law occur, due to the fact that with increasing rate of flow the long molecules lie more firmly parallel, and the resistance of the unordered molecules to the current is diminished.³⁴ These deviations occur only in the region of gel solutions, *i. e.*, where interference of the long molecules takes place.³⁵

The surprising viscosity of a rubber solution is therefore not to be attributed, as Fikentscher and Mark³⁶ assume, to a special solvation of molecules of medium size. Neither does it depend upon a strong solvation of micelles (as assumed by Meyer³⁷) which are formed by a grouping of primary valence chains, but to the great sphere of action of the long molecules.

The table on page 374 shows how the sphere of action of 0.1-molar polyrene solutions changes with increasing molecular length, and how the boundary concentration, that is, the concentration at which a sol solution changes to a gel solution, lies, with increasing molecular length, in the region of constantly more dilute solutions. Thus a 1.0% solution of a hemi-colloidal polyrene is still a dilute sol solution, of which the molecular weight itself has yet to be determined. On the contrary, a rubber solution of the same concentration is a gel solution, which cannot be utilized for molecular weight determinations.

With hemi-colloidal products having numerous small molecules in their solutions, molecular weight determinations can be easily carried out, because such measurements can be made in relatively concentrated solutions. Molecular weight determinations are very difficult with macromolecular products, because there are only a few molecules in solution, and measurements can be made only in the range of great dilution. It is to be expected therefore that osmotic measurements will be only slightly successful. For this reason determinations of molecular weight by viscosity measurements are of especial value.

The following table gives in column 5 the sphere of action of all the molecules of different homologous polymeric polyrenes. The table shows that the sphere of action at constant concentration increases rapidly with increasing molecular size. Column 6 shows which sphere of action the molecule of a 0.1-mol. solution

possesses in relation to the volume of the solution. Finally column 8 gives the boundary concentration at which the sol solution changes to the gel solution.

Product	Approximate Values for Average Molecular Weight	Approximate Values for the Degree of Polymerization	Number of Molecules in 1 Cc. in 0.1-Mol. Solution	Sphere of Action of a Molecule in Cu. A. U.	Sphere of Action of All Molecules in 1 Cc. Solution in Cu. A. U. in 0.1-Mol. Solution	Sphere of Action as % Total Volume of Solution (0.1-Mol. Solution)	Conversion from True Solution into Gel Solution at Concentration	
Raw <i>Hevea</i> rubber..	170,000	2500	2.4×10^{16}	1.5×10^8	3.6×10^{24}	360	0.03	%
Rubber purified according to Pummerer								
Difficultly soluble	68,000	1000	6×10^{16}	2.4×10^7	1.5×10^{24}	150	0.067	0.46
Easily soluble....	54,000	800	7×10^{16}	1.5×10^7	1.1×10^{24}	110	0.09	0.61
Balata.....	51,000	150	8×10^{16}	1.3×10^7	1.0×10^{24}	100	0.10	0.68
Milled rubber.....	27,000	400	1.5×10^{17}	3.8×10^6	5.7×10^{23}	57	0.18	1.2
Hemi-colloidal poly-								
prenes, 1.....	6,800	100	6×10^{17}	2.4×10^5	1.5×10^{23}	15	0.67	4.6
2.....	3,400	50	1.2×10^{18}	6×10^4	7.2×10^{23}	7.2	1.4	9.6
Lower molecular poly-								
prenes.....	680	10	6×10^{18}	6×10^{15}	1.5×10^{23}	1.5	6.7	46.0

3. The Swelling of Rubber

The swelling power of rubber can be explained by its synthesis from macromolecules. This is related to the molecular size, for great differences in the swelling power are observed in the case of homologous polymeric polyprenes, *i. e.*, of various types of rubber, as well as the homologous polymeric polysterols.³⁸ The hemi-colloidal products which have a molecular weight of from 1000 to 10,000 dissolve without swelling. With increasing length of molecule, swelling phenomena appear to an increasing degree during solution, and these phenomena are very considerable in the case of high molecular products having an average molecular weight of 100,000 to 200,000.

These observations are explained in the following way. With hemi-colloidal products the relatively small molecules are quickly dissolved before the solvent can penetrate to the interior of the substance. With eucolloidal products, the macromolecules pass into solution very slowly and the solvent is able to penetrate between the long molecules before the outer molecules are completely dissolved.

This different relation depends upon the joint effect of a series of factors. In the first place the intermolecular forces are much greater with high molecular substances than with low. Because of this fact, high molecular substances are more difficultly soluble than low. With very long molecules a portion of the molecules can be solvated—can be surrounded with a monomolecular layer of solvent—while another part of the molecule is still directly united³⁹ to the next molecule by means of intermolecular force. Furthermore, the velocity with which the completely solvated molecules diffuse into the solvent, becomes less as the molecular length increases. With hemi-colloidal substances the solvated molecule migrates away rapidly, therefore the process of solution can proceed rapidly. With eucolloids, on the contrary, the solvated macromolecules diffuse very slowly and thus there is formed about the solid high molecular substance a highly concentrated layer from which the molecules diffuse out slowly.

This diffusion process is particularly hindered if the concentrated solutions

(1-5%) of macromolecular substances are gel solutions, because they produce sol solutions in hemi-colloidal products. The free movement of the molecule is impeded in a gel solution and diffusion is retarded.

These three factors, the increase in the intermolecular forces with increasing molecular weight, the diminution of diffusion and finally the greater sphere of action of the molecules, retard the process of solution so that the molecules of the solvent have time to penetrate between the molecules of high molecular substances and bring about swelling. In the first stage of swelling, therefore, the parallel orientation of the molecules is not yet lost. A solid gel is still present, which gradually changes to a gel solution in which the molecules are movable, it is true, but are mutually disturbed because the sphere of action of the molecules is greater than the volume at their disposal. Only in very dilute solution, for rubber a concentration of less than 0.5%, is there a true solution, *i. e.*, a sol solution. The process of solution of hemi-colloidal and eucolloidal rubber can be illustrated in the following schematic diagram. (See Figs. 1 and 2.)

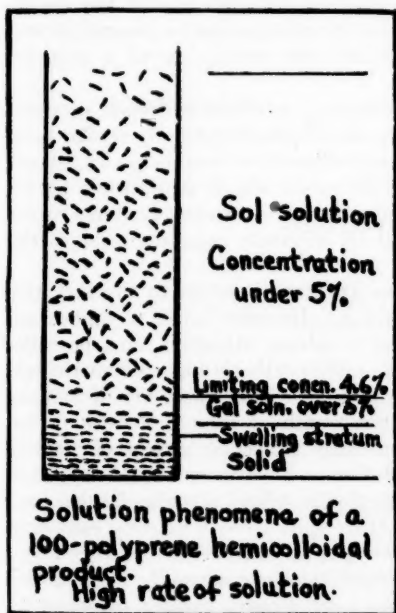


Figure 1

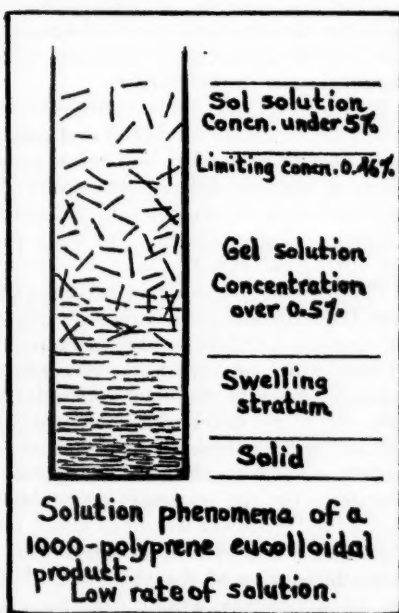


Figure 2

The swelling of rubber is therefore an intermolecular phenomenon, which has already been proposed by Katz⁴⁰ in his well-known work on swelling. Swelling is accordingly no proof that high molecular substances have a micellar structure, as has often been assumed. These observations are valid only for homopolar molecular colloids which have unlimited swelling as does rubber. In substances of limited swelling, as well as with heteropolarous molecular colloids,⁴¹ the relations are more complicated than in the first case.

4. Chemical Transformation to Macromolecules

In order to understand the chemical transformations to macromolecules and their detection by viscosity measurements, it must first be remembered that the

primary colloid particles are macromolecular and not micelles.⁴² This was proved with synthetic eu colloidal polysterol. Because of its stability, the saturated hydrocarbon chains present an especially simple condition. With polysterol solutions the specific viscosity, the height of viscosity which is brought about in a solution by the dissolved substance, is constant for a greater range of temperature, showing that the colloidal particles undergo no change with rise in temperature, and therefore must produce molecules, because in a micellar structure of colloidal particles the specific viscosity would have to change upon heating, since small molecules will be held together only by strong forces in the micelles.⁴³

In viscosity measurements of rubber solutions it is seen that upon standing or shaking the viscosity diminishes, especially upon heating. This change in the viscosity is an indication that the colloidal particles are made up of solvated micelles, as Meyer and Mark have suggested. All viscosity measurements of rubber solutions which are not carried out under especially careful conditions apparently do not make it appear that the decrease is related to the fact that the primary colloidal particles of a rubber solution produce macromolecules, for the specific viscosity changes with other influences. Such changes cannot be reconciled with the idea that macromolecules are primary colloidal particles until a complete explanation is forthcoming.⁴⁴

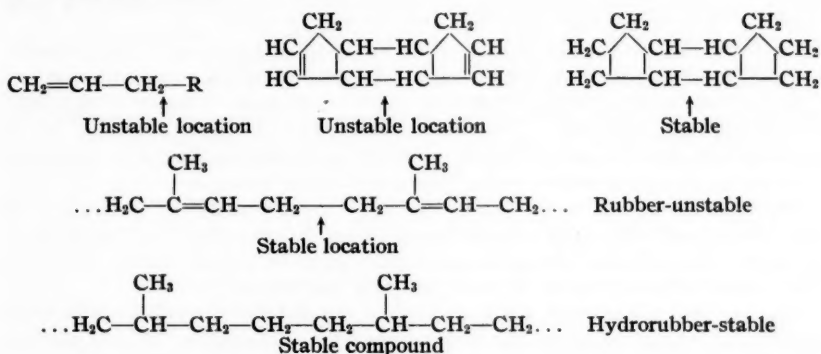
It is, however, not probable from the foregoing that two high molecular products which are so similar as rubber and polysterol, and result from wholly similar processes of polymerization and show many similarities⁴⁵ in their behavior, should show an entirely different structure. The inference was drawn earlier on the basis of similar conclusions that molecules and not micelles are dissolved in a rubber solution. Meanwhile this has been proved by viscosity measurements carried out with great care.⁴⁶

The viscosity changes in rubber solutions are due therefore to the fact that here the macromolecules are especially sensitive. In order better to understand the unusual instability of the macromolecules of rubber, attention must be called to facts which are based on experiments on stable synthetic high polymeric substances, especially the macromolecular polysterols.⁴⁷ The sensitivity of homologous polymeric polysterols increases with the length of their molecules. Thus hemi-colloidal polysterols, which have an average molecular weight of 1000 to 10,000, are still stable upon heating the solution in an atmosphere of oxygen or bromine. On the contrary, eu colloidal polysterols whose macromolecules have an average molecular weight of about 100,000 are split up with extreme ease when the solution is heated in an atmosphere of oxygen or bromine, as evidenced by a great diminution of the viscosity. These diminutions in viscosity suggest that the small molecules arising from the cleavage have a much smaller sphere of action than the original large molecules. Consequently, in spite of a constant concentration the original solution becomes more viscous than that which contains the broken down molecules. Great differences in the macromolecules are recognized by the easily proved differences in the viscosity of the solution, and therefore viscosity studies will in the future play an especially important part in carrying out chemical transformations and changes in the macromolecule.

The increasing instability of the macromolecule with increasing length can be illustrated by comparing the different long molecules of a homologous polymeric series with rods of the same diameter but of different lengths. A wooden rod one meter long and one centimeter diameter is stable, whereas one that is ten meters long is easily broken if it is set in vibration. The molecules must show quite similar behavior. The dimensions of hemi-colloidal molecules correspond to the short rod, those of eu colloidal molecules to the long rod.

The peculiar sensitivity of the rubber molecule in comparison with that of polyesters and other saturated high polymeric compounds depends upon the peculiar chemical structure of the rubber molecule. In this connection the facts which are of importance in rubber chemistry have already been discussed in detail.⁴⁸ However, they must be briefly restated here because until now they have not been taken into consideration.

From many experiments in organic chemistry it is known that the bonding of allyl groups is particularly weak.⁴⁹ Carbon chains which have an allyl group are correspondingly easily broken up. A simple example of this is the cleavage of dicyclopentadiene into cyclopentadiene, while the hydrogenation product of dicyclopentadiene, which no longer possesses an allyl group, is relatively stable.⁵⁰ This allyl group is also found in rubber, where there are therefore molecules of a certain size much less stable than the molecules of equal length of saturated hydrorubber.



For example, a dissolved rubber of average molecular weight of 30,000 (masticated rubber) will, upon heating to 150°, be split into hemi-colloidal decomposition products of a molecular weight of about 3000 to 5000.⁵¹ This is made evident by a pronounced diminution of the viscosity of the solution. Solutions of hydrorubber of the same average molecular weight of 30,000 on the contrary remain stable when heated to 150°, and there is no change in the viscosity of the solution.⁵²

The macromolecules of rubber are especially sensitive to air and oxidizing agents in the cold. Even in a solvent containing air, an oxidative decomposition occurs, resulting in a diminution of the viscosity. Extensive decomposition results from the action of the halogens, hydrogen halide, sulfur chloride, and nitrobenzene.⁵³ A number of investigators have already been surprised by the great diminution in viscosity which rubber solutions undergo upon the addition of these reagents.⁵⁴ This has frequently been attributed to a depolymerization of the rubber, without the idea of depolymerization having been clearly defined. Often depolymerization has been considered a disaggregation of the rubber particles. The concept of depolymerization is, however, to be considered as strictly chemical,⁵⁵ since the process consists of a change of larger molecules into smaller fragments and finally into the monomer. These changes in viscosity do not depend, as Hock thought, upon adsorption and complete absorption of micellar forces through the additions.⁵⁶ In all cases the macromolecules of rubber were first split off by the action of the reagents to hemi-colloidal decomposition products, and only then does transformation occur. Most derivatives of rubber are not derivatives of rubber itself.

but rather of hemi-colloidal decomposition products. Above all there is in the beginning an extensive cracking of the macromolecules of rubber during vulcanization, both with vulcanization in the cold with sulfur chloride and also during hot vulcanization. Accordingly, viscosity measurements of the original rubber permit of no direct conclusions upon the quality of the vulcanizates.⁵⁷

Only with catalytic reduction does one succeed in transposing the rubber molecule in such a way that a relatively slight decomposition occurs. It is therefore possible by carefully hydrogenating rubber and balata in the cold to obtain a high molecular hydrorubber and hydrobalata.⁵⁸

It is remarkable that in many cases not only diminution in viscosity in rubber solutions are observed, but also increases in the viscosity, which bear some relation to the aging of rubber. It was thought that in this process the destroyed micelles could be reconstructed. But these observations also can be explained otherwise, as is done elsewhere. The extraordinarily reactive fiber molecules of rubber can react with one another, with the formation of larger branched molecules, which then produce the increase in viscosity.

Finally with many transformations of rubber, the action of sulfur chloride, sulfur dioxide, more with many oxidation processes, and still more with hot vulcanization with sulfur, there results an extensive linkage of the fiber molecules to 3-dimensional molecules. These are still capable of swelling as long as the linkage is not very strong. When a very strong linkage of these fiber molecules to 3-dimensional molecules results, they are wholly insoluble.

Finally in the case of many rubber syntheses the appearance of insoluble polymers which can only swell are observed. This depends upon the same cause. In this synthesis in the laboratory, a mutual union of the individual fiber molecules occurs with formation of 3-dimensional macromolecules.

The manifold phenomena which the colloid chemist finds in rubber, and which surprise the organic chemist, can be explained in a satisfactory way by the fact that rubber is composed of macromolecules, and that because of their length and their chemical structure these macromolecules are particularly unstable.

Summary

1. The establishment of the molecular size of high molecular compounds which are composed of fiber molecules by the end-group method of determination is only possible if homologous polymeric series of similar type are concerned.
2. The end-group method assures reliable values with molecules up to a molecular weight of 1000 at the highest. With higher molecular products, like cellulose and rubber, the method is inexact.
3. The molecular weight of rubber and balata may be determined by viscosity determinations in the following two ways: (a) $M = \eta_{sp}/cK_m$; (b) $M = K_c \cdot K_{cm}$. The constants K_m and K_{cm} are determined with low molecular decomposition products.
4. Rubber and balata are composed of fiber molecules, which in one dimension have the magnitude of colloidal particles and in both the others, the dimensions of low molecular substances.
5. In highly viscous rubber solutions, there is the characteristic state of solution. As a result, the sphere of action of the dissolved molecule is greater than the volume at the disposal of the solution. This solution is midway between a true solution and a gel, and is therefore designated as a gel solution. It occurs only with high molecular substances, and is characteristic of them.
6. The readiness with which rubber solutions vary is explained by the fact that the rubber molecules are very sensitive to chemical influences and to changes in

temperature as a result of the position of the double bonds. This sensitivity varies with the length of the molecules.

References

- ¹ Communications 24-31, *Helvetica Chim. Acta*, **13**, 1321 (1930).
- ² Pummerer, *Z. Kolloidchem.*, **53**, 75 (1930).
- ³ Staudinger and Signer, *Helvetica Chim. Acta*, **11**, 1048 (1928).
- ⁴ This concept might have been made to agree with the ordinary concepts of colloid chemistry, since highly dispersed particles have greater adsorptive power than less highly dispersed ones.
- ⁵ Staudinger and Lüthy, *Helvetica Chim. Acta*, **8**, 41 (1925); Lüthy, *Thesis*, Zürich, **1923**; Staudinger and Signer, *Ann.*, **474**, 145 (1929).
- ⁶ Staudinger and Lüthy, *Helvetica Chim. Acta*, **8**, 61 (1925); Staudinger and Johner, *Ann.*, **474**, 205 (1929); Johner, *Thesis*, Zürich, **1927**.
- ⁷ Lectures at the Düsseldorfer Naturforscherversammlung, *Ber.*, **59** (1926).
- ⁸ Staudinger, Signer, Johner, Schweitzer, and Kern, *Ann.*, **474**, 246 (1929).
- ⁹ Samec, *Kolloidchemie du Stärke* (Dresden, **1927**), page 29.
- ¹⁰ Particularly well suited are the polyethylene oxides with which Lohmann obtained a molecular weight of 10,000. The molecular weight determined by chemical method agrees with that obtained by the cryoscopic method.
- ¹¹ Staudinger, *Kolloid-Z.*, **51**, 71 (1930).
- ¹² Meyer and Mark in their book on high polymeric organic compounds have incorrectly interpreted the earlier work on this subject. It is self-evident, that the different homologous polymeric series differ greatly from one another in their chemical properties. For example, it is also self-evident that polyoxymethylenes and polyprenes of the same average molecular weight have entirely different properties. The suggestion that one end group, which is small relative to the chain, can greatly influence the reaction of the chain, and that the chemical properties depend upon the end groups, is valid only for the same homologous polymeric series.
- ¹³ Staudinger, *Ber.*, **63**, 921 (1930); *Kolloid-Z.*, **51**, 71 (1930). There was, for example, frequently the doubt (see Pummerer, *Ber.*, **62**, 2628 (1929)) whether molecular weight determinations could be carried out with high polymers. It was assumed that solvation of these long molecules took place, which led to false results. The true situation is, however, simple; molecular weight determinations are possible within the range of sol solutions.
- ¹⁴ Staudinger and Wiedersheim, *Ber.*, **62**, 2406 (1929).
- ¹⁵ Staudinger, *Ber.*, **59**, 3032 (1926); Staudinger, Johner, Schiemann, and Wiedersheim, *Helvetica Chim. Acta*, **12**, 962 (1929).
- ¹⁶ Staudinger, *Ber.*, **59**, 3034 (1926).
- ¹⁷ According to the investigations of Ruzickas on the tension theory of Baeyer, it is probable that the latter is not valid for rings with a higher number of members. Therefore it appears that the formation and stability of such high-membered ring systems is quite possible.
- ¹⁸ Staudinger, Ashdown, Brunner, Bruson, Wehrli, *Helvetica Chim. Acta*, **12**, 942 (1929).
- ¹⁹ For the classification of processes of polymerization, see Staudinger, *Ber.*, **63**, 1073 (1930).
- ²⁰ Brunner, *Thesis*, Zürich, **1926**, page 22.
- ²¹ Bergmann and Machemer, *Ber.*, **63**, 316 (1930).
- ²² For the characteristic end groups of rubber decomposition products, see Staudinger and Bondy, *Ann.*, **468**, 13 (1929); Staudinger and Joseph, *Ber.*, **63**, 2888 (1930).
- ²³ See also the experiments of Staudinger and Freudenberger, *Ber.*, **63**, 2334 (1930), on the molecular weight determinations of acetylcellulose by end groups.
- ²⁴ Staudinger, *Kolloid-Z.*, **51**, 71 (1930).
- ²⁵ Staudinger and Heuer, *Ber.*, **63**, 222 (1930).
- ²⁶ Staudinger and Bondy, *Ber.*, **63**, 734 (1930).
- ²⁷ Staudinger and Nodzu, *Helvetica Chim. Acta*, **13**, 1350 (1930).
- ²⁸ Staudinger, *Ber.*, **63**, 925 (1930).
- ²⁹ Staudinger and Bondy, *Ann.*, **468**, 1 (1929).
- ³⁰ Meyer and Mark, *Ber.*, **61**, 1939 (1928).
- ³¹ Pummerer in *Handbuch der Kautschukwissenschaften* (Leipzig, **1929**), page 267.
- ³² The data of Meyer and Mark (see Note 30) are based on the determination of the size of crystals. Compared with the numerous observations on the synthetic substance, this is not tenable. The significance of x-ray determinations in explaining the constitution of rubber, as generally of high polymers, is often judged incorrectly. The molecular size of high polymers is, on the basis of x-ray studies, not known exactly, either for cellulose or rubber, and the molecular size is the decisive point in an explanation of the constitution, because upon it depend the "high molecular" properties.
- ³³ Staudinger, *Kolloid-Z.*, **51**, 71 (1930); *Ber.*, **63**, 929 (1930).
- ³⁴ Staudinger and Machemer, *Ber.*, **63**, 2924 (1930).

- ³⁵ Unpublished experiments of Heuer.
- ³⁶ Fikentscher and Mark, *Kolloid-Z.*, **49**, 135 (1929).
- ³⁷ Meyer and Mark, *Ber.*, **61**, 1945 (1928).
- ³⁸ *Ber.*, **62**, 241 (1929).
- ³⁹ A solvate shell of homopolar compounds is, according to a study by Staudinger and Heuer, *Ber.*, **62**, 2933 (1929), a monomolecular layer of solvent around the fiber molecule, while Fikentscher and Mark, *Kolloid-Z.*, **49**, 135 (1929), assume it to be a very thick shell, increasing in thickness with increase in the molecular length.
- ⁴⁰ Katz, *Kolloidchem. Beihefte*, **9**, 1 (1917).
- ⁴¹ Staudinger, *Ber.*, **62**, 2893 (1929).
- ⁴² Staudinger and Heuer, *Ber.*, **62**, 2933 (1929).
- ⁴³ The micellar structure of rubber particles. Meyer and Mark, *Ber.*, **61**, 1945 (1928).
- ⁴⁴ Fikentscher and Mark assume that in a rubber solution molecules are present (*Kolloid-Z.*, **49**, 135 (1929)). Mark gives up his view, expressed in his earlier works (see *Ber.*, **61**, 1945 (1928)), without offering any proof that molecules and not micelles are present.
- ⁴⁵ Staudinger, Brunner, Frey, Garbsch, Signer, and Wehrli, *Ber.*, **62**, 241 (1929).
- ⁴⁶ Unpublished studies by Staudinger and Bondy. For proof that balata is dissolved molecularly, see Staudinger and Leupold, *Ber.*, **63**, 730 (1930).
- ⁴⁷ Staudinger, Frey, Garbsch and Wehrli, *Ber.*, **62**, 2912 (1929).
- ⁴⁸ Staudinger, *Ber.*, **37**, 1206 (1927); Staudinger and Bondy, *Ann.*, **468**, 5 (1929).
- ⁴⁹ Braun, *Ann.*, **436**, 299 (1924); **445**, 201 (1925); Claisen, *Ann.*, **401**, 21 (1913).
- ⁵⁰ Staudinger and Rheiner, *Helvetica Chim. Acta*, **7**, 25 (1924).
- ⁵¹ Staudinger and Bondy, *Ann.*, **468**, 1 (1929).
- ⁵² Experiments by Feiszt and Leupold on hydorrubber and hydrobalata. *Helvetica Chim. Acta*, **13**, 1361 (1930).
- ⁵³ Staudinger and Joseph, *Ber.*, **63**, 2888 (1930).
- ⁵⁴ Bernstein, *Kolloid-Z.*, **12**, 273 (1913); Kirchhof, *Ibid.*, **14**, 35 (1914); Spence and Kratz, *Ibid.*, **14**, 262 (1914).
- ⁵⁵ Staudinger and Joseph, *Ber.*, **63**, 2888 (1930).
- ⁵⁶ Hock, *Handbuch der Kautschukwissenschaften*, page 536 (1930).
- ⁵⁷ The attempt has already been made many times to find such relations. Axelrod, *Gummi-Ztg.*, **24**, 352 (1909); de Vries, *Chem. Zentr.*, **1924**, II, 1744.
- ⁵⁸ Staudinger and Feiszt, *Helvetica Chim. Acta*, **13**, 1361 (1930).

Rubber

Part XII.¹ Levulinic Acid Peroxide from Rubber

Rudolf Pummerer, George Ebermayer, and Karl Gerlach

UNIVERSITY OF ERLANGEN

Method of Formation.—The so-called levulinic aldehyde diperoxide, which has already been described by Harries and which we call more correctly "levulinic acid peroxide," is formed not only by "over-ozonization" of the rubber ozonide, but always when rubber ozonide solutions are kept sealed up for a long time, for example, in an ice box. While frequently at first there is only a very slight precipitation after the ozonization, in the course of eight to fourteen days it increases greatly. After filtering and after washing with ether, the yield may reach from 15-20% of the carbon skeleton of the rubber, and it is therefore a decomposition product of the rubber ozonide, which is formed in the neutral medium, perhaps by traces of moisture. Since it is also especially easy to isolate beforehand and is a suitable weighing substance for levulinic acid, we have attempted to confirm for ourselves that the substance still contains the unchanged carbon skeleton of levulinic acid.

Description: Analyses and titrations: The melting point of the crude products is constant and can vary from 173° to above 190°. It is recrystallized from hot water, which is heated for a short time to 100° by the introduction of steam. The melting point is then around 194°, and in a few cases it reached 196°. Massive irregular double-refractive crystalline scales of the approximate composition $C_5H_8O_4$ (already found by Harries), which is, however, double the molecular weight. By solution in caustic soda and reprecipitation with acid, a substance very difficultly soluble in water may be purified. The melting point does not usually change, but such a product exhibits after recrystallization extremely characteristic double-wedge shaped tops on the now elongated regular right-angled scales.

The analytical results are the same as with the compound which was not dissolved in alkali. Our experiments are limited to preparations crystallized from water.

Harries found for "levulinic diperoxide" $C_5H_8O_4$ values of C 45.32, 45.42; H 6.63, 6.26 (calculated C 45.45, H 6.06). We were able to confirm them on the recrystallized as well as the preparation previously dissolved in alkali. C 45.78, 45.42, 45.76, 45.41; H 6.86, 6.26, 6.36, 6.12.

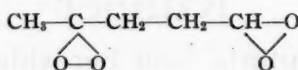
0.0516 g. of substance required 3.90 cc. 0.1 N NaOH, corresponding to 0.0156 g. NaOH or an equivalent weight of 132.5 (calculated for $C_5H_8O_4 = 132$).

The molecular weight determination in boiling alcohol gave 272.5; 0.0194 g. of substance in 3.164 g. alcohol: $\Delta = 0.027^\circ$. This determination explains the double molecular weight (calcd. for $[C_5H_8O_4]_2 = 264$), although in the peroxides association is not impossible. The substance decomposes upon longer boiling in alcohol. The cryoscopic determination in dioxan ($K = 4.950$) gave the values 262.2 and 256.

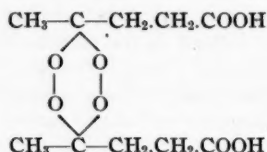
The oxidation value was obtained with titanium trichloride in hot aqueous solution (I) or in a 3-hour reaction in cold alcoholic-aqueous solution (II), and finally after a short heating in alcoholic-aqueous or acetone-aqueous solution (III). The values obtained by methods II and III corresponded to about 1.8 atoms of active oxygen per double molecule; according to I the value reached 1.9 atoms per $[C_5H_8O_4]_2$:

0.0385, 0.0610, 0.0635 g. substance required 5.47, 8.79, 9.23 cc. 0.1 N titanium trichloride solution, corresponding to 4.376, 7.032, 7.384 mg. of active oxygen or 1.87, 1.90, 1.92 atoms active O in the double molecule.

The Nature and Constitution of the Acid.—Harries tried to explain the alkali solubility of the compound which also gives a silver salt by the acid character of the aldehyde-hydrogen atom in the following formula:



The compound is soluble even in cold bicarbonate and can be sharply titrated, in which manner the above formula is obtained, corresponding to an equivalent weight of 132. The reaction is strongly acid, so that doubtless a free carboxylic acid rather than a peracid is involved. As a result, the reaction with hydrogen iodide and titanium chloride was much too sluggish. The conclusion of Harries that Fehling solution is reduced by the peroxide is true of most of the crude products, but not of pure recrystallized preparations, and moreover it is unnecessary to assume the presence of an aldehyde group, even though a peroxide group may be present. On the contrary, the substance gives the iodoform reaction quickly and very strongly. We propose the following formula of a ketone peroxide of levulinic acid:



That the keto groups are placed peroxidically, we assume on account of their inactivity toward 2,4-dinitrophenylhydrazine which, as we found, immediately yielded with levulinic acid in 50% acetic acid orange-yellow needles of dinitrophenylhydrazone, a very difficultly soluble compound which is extremely well suited to the detection and determination² of levulinic acid, m. p. 203° from alcohol. The mother liquors from the recrystallization of the peroxide gave dinitrophenylhydrazone, but only on account of the preceding decomposition of the peroxide to levulinic acid. The determinations of the oxidation value of the peroxide with warm titanium trichloride agreed satisfactorily with the above formula,³ and were only 0.5 as great as according to the old formula of Harries.

Experiments on the synthesis of the peroxide from levulinic aldehyde or levulinic acid and ozone or hydrogen peroxide and HCl (corresponding to acetone-peroxide) had up to now met with no success, not even when hydrogen peroxide in ether was used. This was likewise true of experiments on the preparation of the di-molecular acetone peroxide through ozonide cleavage from acetone and hydrogen peroxide, whereas it often appeared in the ozonization. It has been just as difficult to prepare synthetically the peroxide of azaleic acid semi-aldehyde, which is formed during the ozonization of oleic acid.⁴ Therefore, the failure of synthetic experiments is no proof against our formula.

Reduction Experiments

Of the many reduction experiments which were carried out, we shall describe those which prove the constitution we have chosen.

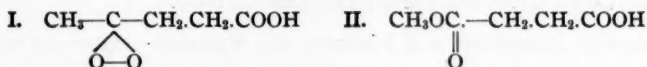
(a) *Reduction with Al-Amalgam in Alkaline Solution to Levulinic Acid.*—In a weakly alkaline solution Al-amalgam is allowed to react with the peroxide until the titanium-sulfuric acid reaction is negative, under which conditions over 90% is precipitable as levulinic acid by means of dinitrophenylhydrazine.

Experiment: 1 g. of the peroxide (m. p. 192°, crystd. from water) was dissolved in 30 cc. water and 1 g. potassium hydroxide and reduced with 2 g. Al-amalgam. After 24 hrs. the peroxide could no longer be detected. It was filtered from the Al sludge, washed, and made up to 100 cc. Twenty-five cc. of acetic acid were added and the dinitrophenylhydrazone of levulinic acid precipitated by a 10% solution of 2,4-dinitrophenylhydrazine in glacial acetic acid. The crude precipitate amounted to 3.23 g., of which, however, 1.0852 g. were insol. in 20% soda (dinitrophenylhydrazine), while the dinitrophenylhydrazone was precipitated from the soda solution with 10% sulfuric acid. The yield of 2.130 g. corresponds to 0.835 g. levulinic acid, which corresponds to 95%. The crude hydrazone melts at 182°; after recrystallization from alcohol, at 201°; crystallized again it melted constant at 203° and gave no depression with the dinitrophenylhydrazone from pure levulinic acid.

4.810 mg. substance: 7.906 mg. CO₂, 1.95 mg. H₂O. 0.154 g. substance: 26.55 cc. N (22°, 729 mm.). Calcd. C 44.50; H 4.05; N 18.95. Found C 44.94; H 4.54; N 18.94.

An earlier experiment carried out in more dilute solution, was continued for a longer time, and yielded only 84% on the levulinic acid. A third experiment gave similar results.

(b) *Reduction Experiments with Titanium Trichloride: Cleavage to Succinic Acid.*—Titanium trichloride in strong HCl solution produces the peroxide very slowly, but on the other hand very quickly when warm,⁵ and here side reactions are not to be overlooked because of the odor of fatty acids (valeric acid (?)). Accordingly the preparation was carried out in the cold and alcohol added in order to keep the peroxide in solution. It must, however, in this case be allowed to stand for a week until the peroxide reaction has entirely disappeared. The result then is no reduction of the peroxide, but cleavage and rearrangement, probably primarily on account of the HCl present. From 1 g. of peroxide there are formed 0.42 g. levulinic acid, as well as a considerable quantity of succinic acid (0.33 g.) and of formic acid (0.28 g.). This means that of the carbon skeleton (0.45 g.) from 1 g. of peroxide there are recovered 48% as levulinic acid, 29.5% as succinic acid and 16.2% as formic acid. It may be said as a basis for the dimolar formula of peroxide that about 0.5 of the molecules change to levulinic acid while the other 0.5 is changed to succinic acid and formic acid by the reaction of the active oxygen. The transformation of ketone peroxides to acid esters was first observed by Baeyer and Villiger⁶ with menthone peroxide. In a similar way from a peroxide having Formula I the monomethyl ester of succinic acid could be obtained by the reaction of acids.



If the peroxide is refluxed with water, small quantities of methyl alcohol can actually be detected in the distillate by the odor and by the benzoic acid ester. The greater part of the methyl alcohol will apparently be oxidized by the peroxide oxygen of the other molecular half to formic acid. The peroxide-O, however, does not suffice. Instead of one molecule, there originate from one molecule of the (calculated dimolar) peroxide 1.6 molecules of formic acid, so that the decomposition of one molecular half follows a still more complicated course than is represented by the above rearrangement. In particular, boiling, and especially with dilute acids, is accompanied not only by rearrangement but by hydrolysis to hydrogen peroxide and levulinic acid. Subsequently this hydrogen peroxide then oxidizes the levulinic acid in a different way. As Matthäus has found, starting with levulinic acid and hydrogen peroxide, boiling produces succinic acid, formaldehyde, formic acid, acetic acid, carbon dioxide, and a little oxalic acid.

Tollens⁷ has already proved that levulinic acid yields these acids with other oxidizing agents. Thus it is easily understood how they are produced by prolonged

steam distillation of the rubber ozonide, which will always yield levulinic acid peroxide. The hydrolysis of the peroxide with boiling water and some organic acid proceeds very slowly by itself,⁸ but rather rapidly on the contrary with the addition of some mineral acid, in which case the hydrogen peroxide can be distilled off (Matthäus).

One gram of the peroxide, m. p. 194° , was dissolved in 100 cc. alcohol in the cold, and to this 20 cc. of titanium trichloride solution and 50 cc. of concentrated HCl were added. This was left standing 50 days until the conversion was completed. The alcohol was then carefully distilled off on a water bath. Ethyl formate passed over with the alcohol, which was shown by the fact that the boiling point of the distilling alcohol dropped to 63° and the distillate had a strong odor of arrak. The distillate had a neutral reaction, and was made up to 50 cc. with alcohol. After evaporation of the alcohol, the excess water of the titanium solution was evaporated. HCl was the chief distillate which passed over. The concentrated peroxide solution was then filtered in order to separate the precipitated titanium oxide. The filtrate was made up to 50 cc.

Ten cc. of the alcoholic ethyl formate were refluxed with 30.39 cc. 0.1 N NaOH for 0.5 hr. After cooling it was titrated back with 18.32 cc. 0.1 N H_2SO_4 . Therefore, 12.07 cc. of 0.1 N NaOH were required to saponify the ester. This corresponds to 60.35 cc. or 0.2414 g. of NaOH, and based on the formic acid to 0.278 g. for the total sample.

At the same time 10 cc. of the liquid were used in a determination of formic acid by the sublimation method. In this case the total quantity required is $0.576 \text{ g. HgCl} \times 5 = 2.88 \text{ g. HCl}$. Recalculated for formic acid, this corresponds to a total of 0.281 g. formic acid.

To determine the levulinic acid formed in one experiment, 10 cc. of the reduced solution were on the one hand treated with 5 cc. of a 3% 2,4-dinitrophenylhydrazine-acetic solution. There was obtained 0.216 g. of hydrazone, m. p. 192° . Calculated on the total quantity, this corresponds to 0.423 g. of levulinic acid.

Independently, 20 cc. of the reduced solution were extracted 3 days with ether in a perforator. Based on the total quantity, there was obtained 0.0857 g. of solid succinic acid after evaporation of the ether. The levulinic acid was again precipitated in the filtrate with 2,4-dinitrophenylhydrazine; 0.943 g. of hydrazone was obtained for the whole sample, corresponding to 0.369 g. of levulinic acid. It appeared, therefore, that the organic acids were even then not completely extracted by the ether. Part of the succinic acid seemed to be still dissolved in the levulinic acid. Therefore, the succinic acid was determined by precipitating the succinic acid from the neutralized acid mixture as a Ba salt, and then a barium determination was carried out on the precipitated Ba succinate. Based on the total quantity, 0.655 g. $BaSO_4$ was obtained, corresponding to 0.332 g. of succinic acid, a quantity which was less than that really present, since the Ba salt does not precipitate quantitatively.

(c) *Reduction Experiment with Platinum and Hydrogen.*—After the conversion to succinic acid in acid solution in the presence of titanium trichloride, we next tried to hydrogenate in neutral medium with platinum and hydrogen the peroxide to levulinic acid in alcoholic solution. No reaction took place in the cold, but, when hot levulinic acid and succinic acid were again formed. Only after this new failure did we turn to the alkaline reduction with Al-amalgam (Expt. a), in order to suppress the conversion completely.

The catalytic hydrogenation was carried out with 1 g. of the peroxide in 200 cc. of absolute alcohol with 0.5 g. of Pt black. Since in the cold no H was used up, it was heated to 70° , where with agitation 280 cc. of H were used up in about 14 hours, being activated once with air during the period. Upon opening, the liquid had a strong odor of acetaldehyde; the reaction with titanium sulfate was negative. After distilling off the alcohol, there remained a liquid that had an ester-like odor, from which pure succinic acid crystallized out upon standing (mixed sample). The equivalent of the oil was 123 (instead of 116 for levulinic acid). It probably consisted chiefly of levulinic acid. No saponifiable substance could be detected.

The present work was carried out with the support of the Notgemeinschaft of the Deutschen Wissenschaften, to whom we express our best thanks.

References

- ¹ Part X, *Ber.*, **62**, 2636 (1929); Part XI, *Kolloid-Z.*, **53**, 75.
- ² The yield of dinitrophenylhydrazone reached 98-99%.
- ³ *Loc. cit.*
- ⁴ A. Rieche, "Alkylperoxides and Ozonides," page 154, Steinkopf, 1931.
- ⁵ Cf. titration of active oxygen above.
- ⁶ *Ber.*, **32**, 3625 (1899).
- ⁷ *Ann.*, **206**, 260 (1881).
- ⁸ After 15 hours' heating of 0.3 g. peroxide in 10 cc. water at 120°, 0.21 g. crystallized out unchanged.

Rubber

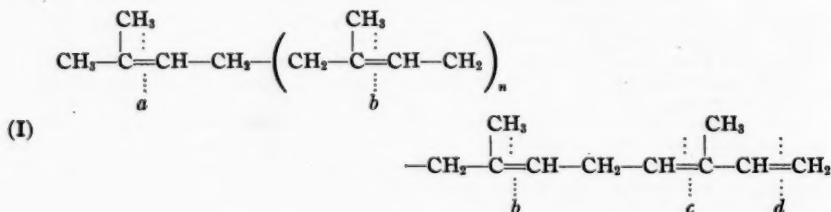
Part XIII¹ The Ozone-Decomposition of Rubber

Rudolf Pummerer, George Ebermayer, and Karl Gerlach

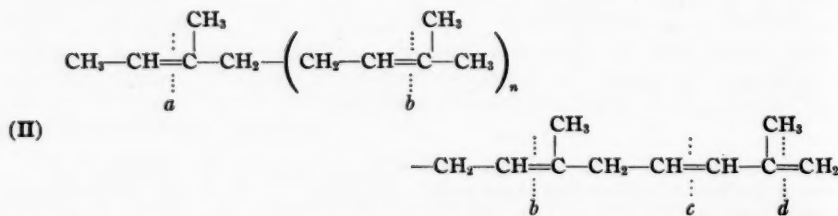
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Theoretical Part. The Work of Harries

Harries and his school have explained the general structure of rubber by establishing the fact that levulinic aldehyde and levulinic acid are the chief decomposition products with ozone. In this way the recurrence of pentadienyl residues: $>C(CH_3)CH_2-CH_2-CH<$ or, as it can be written, of isopentene residues: $-CH_2-C(CH_3)=CH-CH_2-$, in the molecule, and the location of the double bond located near the methyl group, were established. Since Harries could not imagine any cleavage products from the levulinic derivatives he upheld the ring-form recurrence of isopentene residues in the molecule, and opposed the formula of Weber of an open chain. In this case still other cleavage fragments would have to be formed, depending upon whether the first methyl group is located on the second or on the third carbon atom of the chain, according to I or II below:



with *a* acetone, *b* levulinic aldehyde, *c* malonic dialdehyde, *d* methylglyoxal and formaldehyde, and



with *a* acetaldehyde, *b* levulinic aldehyde, *c* acetoacetaldehyde, *d* methylglyoxal and formaldehyde. In place of the aldehyde the corresponding acids could be present.

Formaldehyde and formic acid were indeed found by Harries, but not specifically, since formaldehyde can be obtained by the ozonization of hexane. Acetone and methylglyoxal were not found by Harries, in spite of diligent study and work on

great quantities of rubber, nor was acetic acid found, which replaces acetone in Formula II as the first cleavage fragment (a), as was to be expected. The cleavage of fractions of possible "end members" of an open chain would by their quantity have allowed a conclusion as to the length of the chain, and as to the number of isopentene groups, which at that time were in no case assumed to be above six to eight. The absence of end groups was accordingly the basis for Harries' ring-formula for rubber, while Staudinger later explained the same facts, and also the high viscosity of rubber, by the theory of an extremely long open chain of about 1000 isoprene groups.

The idea that no end groups are to be found is not proved in a satisfactory way, at least at the present time. Harries has obtained from the isolated reprecipitated rubber ozonide having the formula $[C_5H_8O_3]_x$ a very good yield of levulinic derivatives, namely, 95%, when the estimation is favorable. With raw rubber, however, he obtained essentially poorer yields, because resins and losses occurred, so that actually scarcely 70% of the theoretical yield was reached. In order to get the clearest possible idea, and to be independent of the oxygen content of the different cleavage fractions, we calculated, on the basis of the carbon skeleton (in g.) used, the yields obtained by Harries,² and obtained the following results:

	Per Cent
Levulinic aldehyde, expressed as pyridazine	1.24
Pure levulinic aldehyde	10.90
Levulinic acid	44.10
Formic acid	0.56
Succinic acid	0.17
	56.97

Nine and one-tenth per cent remained as the residue of the ozonization. There remained 43.03% of unidentified substance. However, if the crude yield of levulinic aldehyde (154 g.) obtained by Harries is considered (which of course diminishes to one-third upon purification), a yield of 77.7% is calculated.

Since even today very long chain formulas are discussed, it is obviously necessary to improve the yields in the cleavage.³ Also the chemical molecular weight determinations of a very long chain by the aid of end groups lies within the realm of possibility, just as with albumin the titration of the terminal carboxyl and amino groups and recently with carbohydrates the titration of free terminal aldehyde groups with hypiodite, are very important.

The basis for the validity of the conclusions derived from the cleavage fragments on the average length of the rubber chain is that this hydrocarbon contains no structurally foreign impurities, but is built up of homogeneous molecules, though of perhaps different lengths. Since we have at our disposal today pure rubber, and also a number of rubber fractions, it can be determined in some way which cleavage fragment is due to a structural foreign impurity and which is not.

The Ozone Method

In the beginning, by the Harries method, we obtained cleavage of the rubber ozonide by boiling with water and steam-distilling the volatile cleavage fragments. Since, however, secondary reactions occur here, such as oxidation cleavage of levulinic acid and transpositions such as that of levulinic acid peroxide, we have chosen progressively milder conditions. For the decomposition of the ozonide, steam was let in for the shortest possible time, and then the volatile cleavage products were steam-distilled *in vacuo*. Cleavage by steam-decomposition always had advantages for identifying products like acetone. To avoid anomalous cleavage products,

it is, however, better to avoid any rise in temperature, like boiling with water, or even with acetic acid: As a result, after ozonization (which was carried out⁴ in chloroform with 3-4% ozone) we carried out the cleavage process chiefly through reduction either catalytically by the action of Pt black and H (Expt. 3), in which only relatively little H was necessary, corresponding to the experiments of Gottwalt Fischer on phytol, or with nascent H. After eliminating the chloroform in a high vacuum, the cleavage reaction was carried out in moist ether, with calcium shavings and oxalic acid,⁵ or with aluminium amalgam.⁶ During the ozonization, the rubber ozonide remained dissolved, first in chloroform, but large quantities of levulinic acid peroxide separated in crystallized form⁷ on standing in a cold place several days. This offered a very convenient method of weighing one portion of the levulinic acid. If the chloroform is then suctioned off, the ether-soluble ozonide is left behind and is easily reduced. Immediately after isolation by ozonization, it is very difficultly soluble in ether, and must therefore be vigorously agitated in the reduction.

Further improvements in cleavage methods for determining the constitution lie in the direction of rapid, cold, dry working conditions, so that side reactions will be reduced to a minimum.

Individual Experiments

In the present work we have approached very closely the desired goal of an actual quantitative ozonide cleavage of rubber, but it has not yet been fully achieved. The total yield of cleavage fragments, based on the carbon skeleton of the rubber used, reached 95% by careful calculation. We have therefore not limited ourselves to calling any one fraction, according to the boiling point, levulinic aldehyde or levulinic acid, but we have undertaken a determination of the contents of the cleavage solutions by titration and quantitative precipitation with reagents. The latter method made us independent of unavoidable losses in preparation, and permitted us to work with relatively small quantities of rubber (from 5 to 20 g.).

The yields in derivatives of the levulinic series approached 90%. The presence of acetic acid (minimum value up to now 2%) was again observed, of traces of acetone (apparently due to an impurity), and of a substance fermentable by dry yeast (apparently pyroracemic acid). Carbon dioxide and formic acid occurred in from 1-2% (min. 0.9%); succinic acid in varying amounts (0.5-8%), perhaps as a conversion product of levulinic acid peroxide.⁶

The following table gives the results of a number of quantitative cleavage experiments.

Kind of Rubber	Gel-rubber Purified with Alkali		Crepe Sol		Crepe Sol-Rubber Fractions			Total Rubber
Procedure	Steam	Pt + H ₂ in Glacial Acetic Acid	Ca + Oxalic Acid in Moist Ether	Decomposed with Steam			Al- Amalgam	
Quantity Used	10 G.	10 G.	15.8 G.	9 G. Fraction I	6.0 G. Fraction II	6.7 G. Fraction III	20 G.	
Cleavage Fragments:								
1. Carbon dioxide	2.49%	Not detd.	Not detd.	1.68%	1.17%	1.00%	0.91%	
2. Levulinic acid peroxide	17.19%	16.40%	12.40%	16.08%	8.16%	10.75%	17.23%	
3. Formic acid	1.62%	0.53%*	1.74%	1.48%	2.26%	1.93%	1.28%	
4. Acetic acid	12.38%	Not detd.	1.98%	7.96%	7.95%	8.55%	10.05%**	
5. Acetone	Not detd.	Traces	0.05%	
6. Levulinic aldehyde	6.18%	22.50%	25.50%	12.55%	16.45%	10.68%	14.28%	
7. Levulinic acid	42.18%	47.50%	28.30%	42.90%	53.62%	54.50%	49.20%	

8. Succinic acid	0.91%	0.56%	Not detd.	7.24%	4.60%	8.10%	Not detd.
9. Pyrroacemic acid (?)	Not detd.	Not detd.		0.25%	Not detd.	Not detd.	Not detd.
10. Resin, after distillation of the levulinic acid	7.85%	1.73%	Not detd.	Inexact, remained in the cleavage
Without resin	83.58%	89.22%	69.92%	90.14%	94.26%	95.51%	92.95%
% of levulinic residues	67.09%	86.96%	66.20%	78.77%	82.83%	84.03%	80.71%

* Here only the formic acid which was present in the chloroform could be taken.

** The high acetic acid value was not obtained by weighing directly, but was calculated as an impurity in levulinic acid by difference. See Expt. 5c. A part may be succinic acid.

The Individual Cleavage Fragments

Levulinic Aldehyde.—The levulinic aldehyde values in the table refer in all cases, where not otherwise noted, to precipitated microcrystalline methylphenyldihydropyridazine, and many times agree exactly with the values of the Fehling copper number. In many cases deviations occur, which with the copper number amount to +2 to 4% and perhaps depend upon the presence of hydrogen peroxide. The yield of levulinic aldehyde was always, sometimes very much smaller than that of levulinic acid. It varied from 5 to 22%. The steam distillate containing the aldehyde and volatile acids did not color fuchsin-sulfurous acid; therefore, there was no formaldehyde present.

Levulinic Acid.—For the quantitative determination of levulinic acid, which was of especial importance to us as the chief cleavage product we found a good method in the reaction with 2,4-dinitrophenylhydrazine⁸ which, from the aqueous solution, precipitated 98–99% of the levulinic acid present. A comparison of the levulinic acid obtained in the steam-distilled cleavage solution as well as in the distilled fractions with that found by titration, permitted the admixed acetic acid and succinic acid to be determined. The procedure to be used with levulinic acid fractions, especially with the higher molecular acids and the fermentable impurity is, however, not yet settled.

Levulinic Acid Peroxide.—The third form into which the levulinic structure can change by cleavage is levulinic acid peroxide (the earlier levulinic aldehyde diperoxide of Harries), which separates out upon longer standing of the ozonide solution in a 12–20% yield, and is almost insoluble in chloroform. Its constitution is discussed in Part XII, and is established by its reduction to levulinic acid.

The Volatile Acids, Especially Acetic Acid.—The acetic acid overlooked by Harries occurs in the distillate many times in large quantities (5–16%), and is found by titration and subsequent destruction of the formic acid with HgO or chlorine, if cleavage is carried out by the method of Harries with boiling water, and then the volatile acids and levulinic aldehyde are driven off. The destruction of the formic acid is carried out with a concentrated mixture of the sodium salts. The carbon dioxide is absorbed in the crude soda-lime during cleavage.

The great deviations in the acetic acid figures signify that a side reaction is playing a part. It consists of the oxidation of levulinic acid, probably by hydrogen peroxide and other peroxides, to acetic acid and malonic acid or malonic aldehyde acid, which have not hitherto been thought about. The latter might by decomposition lead to more acetic acid. The high acetic acid values with long boiling of cleavage solutions diminish if the volatile acids are driven off *in vacuo*. In that case, correspondingly more levulinic acid is obtained. However, a small % (2–4%) of acetic acid occurs also in the cleavage by reduction, so that it is doubtful whether all the acetic acid originates in side reactions. Further experiments must show whether by still more rapid and more careful work the acetic acid figure may be fur-

ther decreased. For the present it appears to us possible that the low acetic acid number of 2% may originate in an end member: $\text{CH}_3\text{CH} < \text{or} > \text{C}(\text{CH}_3).\text{CH}:\text{CH}_2$, through decomposition of methylglyoxal peroxide, which is easily decomposed⁹ into formic acid and into acetic acid. Stoichiometric relations between the quantities of acetic and formic acids found or between the fraction number of sol-rubber and the quantity of acetic acid, have not been established.

Study of Methylglyoxal or Pyrroacemic Acid.—Harries states that he never ran across methylglyoxal in the decomposition of rubber, though he had sought it especially, and though this substance is easily detected as osazone, which forms during ozonization. Nor have we been able to obtain any methylglyoxal, though the water distillate had the characteristic empyreumatic odor, exactly like methylglyoxal.¹⁰ However, in the ozone-decomposition of carotin also, where it must be formed in large quantities, we have not yet been able to isolate any methylglyoxal. From this we conclude that it must be even more difficult to detect than has been supposed. Because of the great importance of the end group $>\text{C}(\text{CH}_3).\text{CH}:\text{CH}_2$ in identifying methylglyoxal, we have sought above all the supposed oxidation product, pyrroacemic acid. Since levulinic aldehyde, for the greater part, is converted into its acids during the cleavage, this might also be the case with methylglyoxal.

An indication of the presence of pyrroacemic acid in the concentrated levulinic acid solutions, which is also present in smaller quantities in the aqueous distillate and in many fractions of the distilled levulinic aldehyde, is that from these liquids carbon dioxide is liberated by dry yeast (Neuberg). From 2 cc. of levulinic acid solution a few tenths of a cc. of CO_2 were liberated with acetate-buffer at p_{H} 5, so that 6 cc. were obtained from 12.5 g. of rubber. With the small quantities, however, most of the carbon dioxide formed is dissolved in the buffer liquid, as a parallel experiment showed, so that an approximate quantitative determination of the carbon dioxide is not possible. If one wishes to attribute the carbon dioxide actually measured by analysis as rising from pyrroacemic acid, then 0.088% of the carbon skeleton would be accounted for in this way. The corrected values based upon the solubility of carbonic acid which are under consideration would be essentially higher (over 1%). With yeast, levulinic acid gives no trace of carbon dioxide.¹¹ The chemical detection of pyrroacemic acid, as well as the greater part of levulinic acid, could not be well established with phenylhydrazine or even with *o*-phenylenediamine as quinoxaline (m. p. 245.5°, Hinsberg¹²). We obtained turbidity with both reagents, with *o*-phenylenediamine in one case a crude precipitate with an ill-defined melting point around 220° which, because of its small quantity, could not be purified. In blank experiments with a mixture of much levulinic acid and very little pyrroacemic acid, these precipitates were again uncertain.

Acetone.—Harries has also been unsuccessful with acetone, when he tried to isolate this substance from the distillate of the cleavage by column rectification. We proceeded similarly, except that we tested qualitatively for acetone the first 5 cc. which passed over in the rectification. Both the indigo test with *o*-nitrobenzaldehyde and the formation of dibenzalacetone were distinctly positive. The latter reaction was better adapted to the small quantity (a few mg.), and yielded about 80%, while with indigo formation in such a dilution often only 5–20% was obtained.

The yield of acetone reached a maximum of 0.45%, and acetone peroxide could not be proved at all. Once when the rectification was run for a longer time with sulfuric acid in a sealed tube heated at 120°, the yield of acetone was distinctly greater, in other cases not. It seemed important to us that the first and second fractions of a sol-rubber from crude crepe yielded acetone and the third fraction did not. Also, the rubber fractions extracted with ether from gel-rubber yielded no

acetone. Therefore, we believe that the acetone originates in an ether-soluble impurity of the rubber.

Concluding Remarks

The generally accepted theory of Harries that rubber is built up by a succession of isoprene groups: $\leftarrow\text{CH}_2-\text{C}(\text{CH}_3)=\text{CH}-\text{CH}_2\rightarrow$, has received a strong confirmation by the nearly quantitative work on the cleavage product, since now nearly 90% (compared to the earlier 70%) of the carbon skeleton in the form of derivatives of the levulinic series (aldehyde, levulinic acid peroxide) can be obtained.

Harries' statement that no cleavage products with less than five carbon atoms were to be obtained, which might indicate end members of an open chain, is not upheld, since we were able to prove at least 2% of the carbon skeleton in the form of acetic acid in preliminary separation of levulinic acid peroxide and reduction of the ozonide. Under such conditions the secondary formation of acetic acid from levulinic acid appears less probable than by the ordinary methods of working with steam, in which much more acetic acid is formed. Besides acetic acid, another cleavage product was found which had not been observed before. It is contained in levulinic acid as an impurity, is fermented by yeast and is possibly succinic acid. The origin and nature of this cleavage product, like the origin of acetic acid, still remains uncertain. Today neither one can be classed as a definite "end group." It cannot be asserted, however, that no end groups are detectable, and instead the question is still an open one. Its solution appears quite possible with further improvement in the method now in use.

To the Notgemeinschaft of the Deutschen Wissenschaft we extend our best thanks for the assistance which they have given us in carrying out this work.

Description of the Experiments

1. Ozonization of Crepe Sol-Rubber. Fractions 1, 2, and 3 and Cleavage with Steam

The sol-rubber from crepe used in the three experiments summarized here was prepared in the following manner. Fifty grams of crude crepe rubber, which was not extracted with acetone for the removal of resins in this case, was treated immediately with 5 l. of pure ether by stationary extraction. After standing 24 hours, the first fraction was removed, and it yielded 9 g., which were somewhat yellow. After filling up the flask with fresh ether and standing forty-eight hours longer, the second fraction was removed; this was fairly pure white, and yielded 6.5 g. of rubber. The third fraction was removed after standing for eight weeks. This yielded 6.7 g.

The individual fractions were ozonized separately in the usual way. Nine grams of the first fraction in 200 g. of chloroform were treated with 3.7% ozone, 6 g. of the second fraction were treated in 150 g. of chloroform, and 6.7 g. of the third fraction in 150 g. chloroform. After ozonization and evaporation of the chloroform, there remained, with fraction I, 16.5 g. of ozonide, with Fraction II, 15.0 g., and with Fraction III, 11.9 g. Before the evaporation of the chloroform, 1.8454 g. of levulinic acid peroxide (16.08% of the carbon skeleton of the rubber used), 0.9507 g. (8.16% of the carbon skeleton) and 1.3833 g. (10.75% of the carbon skeleton) at 0° were precipitated and filtered off.¹³ The working up of these three experiments was carried out by cleavage with steam in a slow stream of nitrogen. The quantity relations of the cleavage fragments obtained are summarized in the Table.

As an example of this working up of a fraction, Fraction I may be described more in detail.

The ozonide (11.9 g.) was covered with 50 cc. water and then steam and nitrogen were introduced. The carbonic acid formed by the cleavage was carried over into a weighed soda-lime tube. The cleavage was not carried out too rapidly, so that the carbonic acid was thoroughly dried and was completely absorbed. The apparatus was arranged in the following manner.¹⁴ The cleavage receptacle consisted of a ground-glass flask with a tube for the introduction of gas, and above this was mounted a trap for drops. From this the vapors went to a descending coil condenser and into an ice-cooled receiver. The liquid which had passed over was removed from this by a siphon. In addition, a spiral condenser, which was enlarged at the bottom, was connected to the receptacle. The carbonic acid was drawn off through this into a calcium chloride tube and then into a soda-lime tube, which was closed from the outside by a tube containing calcium chloride and soda-lime. The flask used for the cleavage was placed in an oil bath, which was heated at first at 105° and then gradually higher until at the end it reached 130°.

The first 65 cc. which passed over were tested for acetone by still further rectification with a small column. The first 5 cc. passing over of the third fraction contained no acetone, whereas it could be detected in Fractions I and II.

Three hundred and fifteen cubic centimeters of the distillate of the cleavage solution were driven over, which contained the volatile acids. The residue contained 50 cc. of levulinic acid. 0.2123 g. (1% of the carbon skeleton) of carbon dioxide was absorbed in the soda-lime tube.

Determination of the Volatile Aldehydes and Ketones.—The determination of acetone was carried out both with *o*-nitrobenzaldehyde, in which case indigo was used as the weighing substance, as well as with benzaldehyde, in which case even with very low concentrations the yield of dibenzalacetone was about 80%. The first method with *o*-nitrobenzaldehyde gave very poor yields.

To determine the acetone, the first 5 cc. which were carried over by the rectification described above were treated with 5 cc. of a 10% benzaldehyde solution in alcohol and a few drops of a 30% solution of potassium hydroxide. In the case of the third fraction no dibenzalacetone was formed; with the second, after standing a little while this compound separated out as yellow crystals. Some resinous impurity could be separated by washing with cold ether. 0.016 g. of dibenzalacetone, m. p. 111°, was obtained, corresponding to 3.9 mg. acetone, or 0.045% of the carbon skeleton of the rubber used.

After the total distillate had been made up to 500 cc. in a measuring flask, the levulinic aldehyde was precipitated in an aliquot part (50 cc.) with about 10 cc. of a 10% solution of phenylhydrazine in 50% acetic acid. The methylphenyldihydropyridazine separated out very rapidly in yellow flakes. After calculating the total quantity, 1.81 g. of pyridazine were obtained, corresponding to 1.05 g. levulinic aldehyde, corresponding to 10.68% of the carbon skeleton.

In a parallel determination of the levulinic aldehyde with Fehling solution, 1.41 g. of aldehyde were obtained, corresponding to 14.45% of the carbon skeleton. We consider this value rather unreliable, since hydrogen peroxide reacts with Fehling solution, and is usually detected in the distillate. The presence of formaldehyde in the distillate was tested with fuchsin-sulfurous acid. No coloration occurred. It is important to take up the pyridazine precipitate with freshly distilled phenylhydrazine immediately after the cleavage with steam. In this case the pyridazine precipitated immediately in a neat solid form, m. p. 188°, and recrystallized from alcohol 196° (uncorrected), whereas if the distillate is allowed to stand a longer time only oily precipitates could often be obtained.

Determination of the Volatile Acids.—The acids contained in the chloroform which was distilled off were agitated with water, and the aqueous solution titrated. 0.0264 g. of NaOH were used, corresponding to 0.0304 g. formic acid. To neutralize the steam distillate, 0.6757 g. of NaOH were required. The volatile acids contained in the latter were separated into acetic acid and formic acid by the HgO method. After decomposition of the formic acid, the acetic acid was driven over, and 0.324 g. of NaOH were used, corresponding to 0.486 g. acetic acid, *i. e.*, 3.3%. With formic acid 0.352 g. NaOH were used, corresponding to 0.405 g. formic acid, therefore, with formic acid from chloroform 0.4354 g. (1.99% of the carbon skeleton).

Determination of the Non-Volatile Acids.—For the complete titration of the contents of the flask, 2.65 g. NaOH were used. The levulinic acid in solution was determined as 2,4-dinitrophenylhydrazone. Here, too, the residual solution in the measuring flask was made up to a certain volume, and an aliquot part precipitated with a solution of dinitrophenylhydrazine in 50% acetic acid, after the residual solution had been standardized to 50% acetic acid by the addition of glacial acetic acid. An excess of about 20% of dinitrophenylhydrazine is suitable. There is precipitated, besides the dinitrophenylhydrazone of levulinic acid, free dinitrophenylhydrazine or its acetyl derivative. Therefore the crude precipitate is dissolved as much as possible in a 20% soda solution, filtered, and again acidified with dilute H_2SO_4 , whereby the dinitrophenylhydrazone of levulinic acid precipitates out fairly pure in orange-yellow flakes. This product was filtered off, dried in vacuum and weighed, m. p. 198° after recrystallization from 60% alcohol at 203° . The third fraction of crepe sol-rubber yielded 15.75 g. of hydrazone, corresponding to 6.2 g. of levulinic acid (54.50% of the carbon skeleton). In the total titration above, 2.65 g. of NaOH were used; accordingly 2.14 g. NaOH were required for the levulinic acid, so that 0.51 g. NaOH was accounted for by the slight losses in the levulinic acid precipitate, or as succinic acid, or by acetic acid. Calculated as succinic acid, 0.75 g. were obtained, 0.765 g. as acetic acid (5.25% of the carbon skeleton). It is extremely improbable that after the preceding steam-distillation nearly as much acetic acid is still left in the residue. To be sure, a complete driving-over of acetic acid by the addition of phosphoric acid has not been carried out, so that the titration of the non-volatile acids could be more accurately done. The method of determination of succinic acid as barium salt is still being worked out. In any case, it is not yet completely clear which acids have neutralized the 0.51 g. of NaOH. A small quantity of pyrrolic acid may also play a part here; however, if this acid is precipitated out with dinitrophenylhydrazine it would be calculated with the levulinic acid.

The formation of resins during cleavage of ozonide is, in general, insignificant. In the decomposition of the ozonide of rubber Fraction I, however, 3.076 g. of resin were obtained, from which by boiling was removed 0.982 g. levulinic acid peroxide. In another instance we were convinced that the resin was for the most part dissolved by further treatment with ozone in warm water. On cooling levulinic acid was also formed in larger quantity and of great purity. The formation of resin can therefore under the circumstances not result from an extensive ozonization or cleavage. We have carried over ozonization to the point where a removed sample of the chloroform solution was stable for two minutes to bromine.

2. Ozonization of Gel-Rubber and Cleavage with Steam

In order to establish whether the gel-rubber yielded the same cleavage fragments in the same quantity as sol-rubber, 10 g. of alkali-purified gel-rubber were dissolved in 500 g. of purified chloroform, let stand eight days, and ozonized with 3.75% ozone for 72 hours until stable to bromine. Toward the end of the reaction a considerable quantity of levulinic acid peroxide separated (3.33 g., i. e., 17.19% of the carbon skeleton). After evaporating the chloroform *in vacuo* there remained 18.98 g. of ozonide, and in the distilled chloroform volatile acids were again present. After the acid had been shaken with water, there was 0.291 g. (0.86% of the carbon skeleton) of formic acid, determined by the use of 0.2534 g. of NaOH. Often some HCl appeared; in such cases the formic acid value was corrected by a chlorine determination.

The ozonide was decomposed as in Fraction I with steam in a current of nitrogen, by which 0.803 g. CO_2 (2.49% of the carbon skeleton) was evolved. The first 50

cc. of the distillate were separated as in Fraction I, further purified and tested for acetone with negative results. One thousand cubic centimeters of water were distilled over, containing the levulinic aldehyde and volatile acids. A further 500 cc. were driven over at a temperature on the oil bath of 130°. The residue was distilled *in vacuo*, yielding the following fractions (12 mm. pressure):

	Fraction	Internal Temp.	Temperature of Heating	Height	Remarks
I.	Colorless	70–100°	125°	25 cc.	Chiefly water and acetic acid
II.	Yellow-brown	100–120°	143°	0.30 g.	Levulinic acid
III.	Yellowish	138–140°	175°	4.75 g.	
IV.	Brownish	125–128°	180–200°	1.95 g.	
V.	Brown residue	100°	200°	1.70 g.	

More acids could be extracted from the residue by boiling with water. Then there still remained 1.132 g. (7.85% of the carbon skeleton) of residual resin. This is greater than the yield from similar experiments with sol-rubber.

Volatile Acids.—1.486 g. of NaOH were required to neutralize the acids which passed over with the steam. The solution showed, however, a high after-titration, since 0.354 g. additional NaOH was required for final neutralization. This after-titration might be attributed to the presence of α -angelic lactone, which may form during the slow distillation of levulinic acid solutions. Therefore this portion was calculated as levulinic acid (1.025 g.), since the lactone is also decomposed to levulinic acid again. The total calculated yield of levulinic acid reached 7.32 g., corresponding to 42.81% of the carbon skeleton of rubber.

The separation of acetic acid and formic acid was so carried out that besides the amount of NaOH used only the formic acid was determined. The acetic acid was obtained from the difference. For the determination, an aliquot part of the neutralized distillate was repeatedly shaken with purest ether to remove the levulinic aldehyde, then evaporated and the sodium salt utilized for the determination of formic acid. The sublimation method¹⁹ was used, since the carbon monoxide method¹⁶ did not prove very reliable in a series of control experiments. 500 cc. of the acid distillate were evaporated after neutralization and ether extraction, the sodium salt was treated with 40 cc. of 5% sublimate solution, 5 g. sodium acetate and 40 cc. of water, and refluxed 3 hours on a briskly boiling water bath. The HgCl which separated amounted to 0.132 g., corresponding to 0.1285 g. of formic acid for the 500 cc., and 0.257 g. formic acid (0.76% of the carbon skeleton) for the total distillate (1050 cc.), corresponding to 0.223 g. NaOH. For acetic acid there remained 1.263 g. NaOH in the total distillate, corresponding to 1.890 g. acetic acid. The 500 cc. distilled off at 130° contained only acetic acid, which required 0.407 g. NaOH for neutralization, corresponding to 0.612 g. acetic acid. Much acetic acid therefore originated during the long distillation and heating at high temperature.

The Non-Volatile Acids.—The first fraction precipitated as above with vacuum distillation contained considerable water and also HCl. After removing the HCl present, there still remained 0.140 g. NaOH for the original acid. The acid present was acetic acid, with a yield of 0.21 g., so that the total acetic acid of 1.890 + 0.612 + 0.210 = 2.712 g., corresponding to 12.38% of the carbon skeleton.

The second fraction required 0.045 g. of NaOH and yielded 0.132 g., calculated as levulinic acid. Fraction III required 1.408 g. of NaOH, corresponding to 4.10 g. levulinic acid. 0.58 g. of NaOH were required to neutralize Fraction IV, corresponding to 1.695 g. of levulinic acid. Since 0.20 g. of succinic acid crystallized from this fraction (0.91% of the carbon skeleton), there remained 1.495 g. for levulinic acid, which naturally still contained some succinic acid. From the resinous residue of the distillation, there was extracted a quantity of levulinic acid corresponding to 0.195 g. of NaOH, that is, 0.568 g. of levulinic acid. The total levulinic acid, 7.32 g., corresponded to 42.81% of the carbon skeleton. The undissolved

resin (1.132 g.) was brown, easily pulverized, and contained 61% C and 5.6% H, which are similar to the values arrived at with levulinic aldehyde. The resin obtained constituted 7.85% of the carbon skeleton, an amount which is not found with sol-rubber. Ordinarily only 2-3% of the carbon skeleton remains behind as a resin under similar operating conditions.

3. Ozonization of Gel-Rubber and Cleavage with Platinum and Hydrogen in Acetic Acid

Ten grams of alkali-purified gel-rubber were dissolved in 500 cc. of chloroform and treated while ice-cold with a 0.2% ozone current until stable to bromine (264 hours). The solution was let stand 72 hours in the ice box, whereby a further large quantity of levulinic acid peroxide (3.194 g., corresponding to 16.4% of the carbon skeleton) separated. After the removal of the chloroform by distillation *in vacuo*, there remained 14.25 g. of fairly white viscous liquid ozonide.

The ozonide liberated in high vacuum from the last chloroform residue was dissolved in 50 g. of glacial acetic acid, 0.5 g. of activated platinum black was added, and hydrogenated in an agitator. After 6 hours only 180 cc. of hydrogen were consumed, and after 24 hours 300 cc., after which there was no further absorption. The reaction with titanium-sulfuric acid was now negative, and after filtering off the catalyzer, there remained a clear brown solution which was distilled *in vacuo* at 12 mm.

	Temperature	Weight, G.
Fraction I	To 70°	40
Fraction II	70-80°	5.4
Fraction III	80-160°	5.8
Residue	160°	1.1

Since in Fractions I and II acetic acid was naturally present, it was not determined in this experiment on the determination of the volatile acids (with the exception of formic acid of the chloroform, 0.179 g. or 0.53% of the carbon skeleton). Fraction I was diluted to 100 cc., and with phenylhydrazine it yielded 1.90 g. of pyridazine, which corresponded to 1.105 g. of levulinic aldehyde. This value was obtained with one-half the quantity of the diluted fraction (50 cc.), and was calculated for the whole. The other 50 cc. were used in an experiment with *p*-nitrophenylhydrazine, which yielded, however, only 0.150 g. of orange-red crystals of a *p*-nitrophenylhydrazone. The latter was soluble in methylalcoholic KOH solution, with a deep blue color. Obviously much of the hydrazone remained dissolved in the dilute acetic acid.

The pyridazine determination of Fraction II was unsuccessful, but a parallel determination with *p*-nitrophenylhydrazine yielded 0.6 g. of nitrophenylhydrazone. According to analysis, no homogeneous substance appeared to be present. In conjunction with the results with Fraction I, it must be concluded that 2.21 g. of levulinic aldehyde were present.

The total yield of levulinic aldehyde amounted to 3.315 g., or 22.5% of the carbon skeleton.

The third fraction, after standing a greater number of days, yielded 0.123 g. (0.56% of the carbon skeleton) of succinic acid, m. p. 183°. The filtrate was dissolved in 100 cc. of ether, and after evaporation was again rectified. Two fractions were obtained from this, the first passing over at 70°/12 mm., 0.9 g., equivalent weight 122.5. The second boiled at 124°/10 mm., 4.7 g., equivalent weight 97.4. The residue of 0.85 g. in the flask showed the equivalent weight of 137. The equivalent weight of Fraction II is obviously lowered by succinic acid. Since a precise succinic acid determination is not yet available, both fractions were calculated as levulinic acid from the NaOH used, which gave 0.853 and 5.6 g., respectively, of levulinic acid. The residues of both distillations were extracted with water, and

yielded 0.816 g. (Distillation I) and 0.812 g. (Distillation II) of levulinic acid. 0.25 g. of resin (1.73% of the carbon skeleton) remained insoluble, *i. e.*, essentially less than in the cleavage by hydrogen. The total levulinic acid was calculated at 8.08 g., corresponding to 4.19 g. carbon, or 47.5% of the carbon skeleton.

4. Ozonization of Crepe Sol-Rubber and Cleavage with Calcium and Oxalic Acid in Ether Solution

Fifteen and eight-tenths grams of cold crepe sol-rubber extracted with acetone were treated with 6.8% ozone after 14 days' solution in 400 g. of chloroform. After 72 hours it was stable in bromine, after standing 96 hours longer in the ice box, 3.807 g. of levulinic acid peroxide (12.4% of the carbon skeleton) were filtered off. After evaporation of the chloroform, there remained 27.95 g. of a pale yellow viscous ozonide. This was suspended in 150 cc. of moist ether, since it is difficultly soluble, and to this emulsion was added a solution of 27 g. of anhydrous oxalic acid in 150 cc. of moist ether. The solution was placed in a flask, with a reflux condenser and a stirrer, with 12 g. of calcium shavings. A lively reaction set in immediately, and lasted 6 hours. At the end it was heated for a short time at 40°. Since it still gave a positive titanium reaction, 5 g. of calcium and 3 g. of oxalic acid were added. After standing for 6 hours longer, the titanium reaction was now negative. It gave toward the end an alkaline reaction, on account of a slight excess of calcium and a strong brown coloration of calcium sludge, which unfortunately signified a resinification of levulinic aldehyde. In repeating the experiment, the oxalic acid should be kept in excess. In spite of resinification the experiment is remarkable on account of the large yield of levulinic aldehyde and on account of the small quantity of acetic acid that is formed.

Determination of Levulinic Aldehyde.—The pale yellow ether solution was filtered off from the calcium sludge and evaporated *in vacuo*. 0.699 g. of a sirup-like residue remained, which gave the reactions for levulinic aldehyde. The calcium sludge was extracted with alcohol to remove the absorbed levulinic aldehyde. On evaporation this left behind 5.25 g. of a sirupy yellow substance which, as above, was calculated as (crude) levulinic aldehyde. The total determination of the aldehyde by the Fehling method yielded 8.5 g. Cu_2O , corresponding to 5.959 g. of aldehyde or 25.5% of the carbon skeleton.

Determination of the Volatile Acids.—The calcium salt, washed with alcohol, was boiled with water in order to separate the acids it contained from the precipitated calcium oxalate. The aqueous solution was then treated with 20% H_2SO_4 until no more precipitation occurred, filtered off from the calcium sulfate, and steam-distilled. The volatile acids required 1.269 g. of NaOH, and on evaporation there remained 2.5 g. of sodium salts which, by the HgO method, were determined as 0.933 g. of formic acid (1.74% of the carbon skeleton) and 0.69 g. of acetic acid (1.98% of the carbon skeleton).

Determination of Levulinic Acid.—To obtain the levulinic acid, an aliquot part of the liquid, a total of 750 cc., which was left after the steam distillation and which contained H_2SO_4 , was titrated to determine the total acids. 102.6 g. of NaOH were required to neutralize this. A H_2SO_4 determination was then carried out with a definite portion. The total quantity contained 122.23 g. of H_2SO_4 , which required for neutralization 99.98 g. of NaOH, so that 2.62 g. of NaOH remained for the levulinic acid, corresponding to 7.6 g. (28.30% of the carbon skeleton) of levulinic acid.

5. Ozonization of Alkali-Purified Total Rubber and Cleavage with Al-Amalgam in Moist Ether

Twenty grams of total rubber were dissolved in 500 g. chloroform and were treated with 2.14% ozone until stable to bromine. It was left 21 days in the ice

box with exclusion of air and moisture and filtered off from 6.675 g. of levulinic acid peroxide (17.23% of the carbon skeleton). After the evaporation *in vacuo* of the chloroform containing 0.189 g. of formic acid, there remained 37.3 g. of ozonide. In this experiment the carbon dioxide formed was decomposed in a slow stream of nitrogen. As a result of long standing, the ozonide was then soluble in ether. The titanium reaction was still positive, however. The ozonide was dissolved in 200 g. of ether, 40 cc. of water and 20 g. of Al-amalgam were added. The reaction began moderately, increased gradually, and was completed after about three hours. The absorbed carbon dioxide was determined in a soda-lime tube, giving 0.5844 g. (0.9% of the carbon skeleton). After completion of the reaction, the ether was filtered from the Al salts, evaporated, and the residue rectified. Up to 62°, 0.1524 g. passed over, which gave no acetone reaction. From 68°–72°, 1.7056 g. of acid liquid passed over, and from 145°–150°, 3.3197 g. of almost pure levulinic acid. The titration showed the equivalent weight of 127 (calculated 116). Based on a consumption of 1.0732 g. of NaOH, 3.117 g. of levulinic acid were assumed to be present. The second fraction consisted of formic acid (0.123 g.), acetic acid (0.472 g.), and levulinic acid (0.555 g.).

The Al salts separated from ether were dissolved by heating with water at 60°, filtered from the Al hydroxide formed, and the filtrate was made up to 500 cc. in a measuring flask. 7.696 g. of NaOH were required to neutralize the total quantity. No organic components could be determined in the Al hydroxide. A determination of the Al of Al salts in solution showed that 1.575 g. of Al were combined with the organic acids.

Strange to say, the levulinic aldehyde adhered to the wet Al sludge and to the solution of Al salts obtained from it. Aliquot parts of the solution were tested for levulinic aldehyde, both with phenylhydrazine and with the Fehling method. The phenylmethyldihydropyridazine obtained (7.208 g.) was micro-crystalline, and corresponded to 4.189 g. of levulinic aldehyde (14.28% of the carbon skeleton). The determination of the Cu number gave 5.98 g. of Cu_2O , corresponding to 4.175 g. of aldehyde, which agreed very well with the other determinations.

(a) *Separation of Acids by Steam Distillation in Vacuo.*—Twenty-five cc. of aqueous solution were treated with 5 cc. of 4.38 N H_2SO_4 and distilled *in vacuo*. The volatile acids passing over at 40°/12 mm. required 1.636 g. of NaOH, based on the total weight. After the sodium salt was isolated, the acetic acid (2.16 g.) and formic acid (0.23 g.) were determined¹⁷ by the HgO method. The residue of the vacuum distillation was agitated repeatedly with ether, and was salted out with ammonium sulfate. After evaporation of the ether, 0.2184 g. (0.50% of the carbon skeleton) of succinic acid, calculated for the total quantity, crystallized out. The amount of levulinic acid after titration amounted to 16.87 g.

A parallel experiment of vacuum distillation without previous acidification with H_2SO_4 yielded approximately the same quantity of volatile acids and levulinic acid.

(b) *Separation of Acids by Ordinary Steam Distillation.*—Ten cc. of 4.38 N H_2SO_4 were added to 25 cc. of aqueous Al salt solution and distilled with water as usual. The volatile acids required, calculated on the total amount, 2.47 g. of NaOH which were divided into 0.552 g. of formic acid and 2.99 g. of acetic acid. The residue from the distillation required, after subtracting the quantity of alkali for the H_2SO_4 , 5.22 g. of NaOH for the org. acids, which corresponded to 15.15 g. of levulinic acid.

(c) *Determination of Levulinic Acid as 2,4-Dinitrophenylhydrazone.*—Twenty-five cc. of the Al salt solution were again used, and were first treated with steam to remove the levulinic aldehyde. The residue in 50% acetic acid was treated with dinitrophenylhydrazine, whereby 1.6636 g. of levulinic acid dinitrophenylhydrazone

were precipitated, corresponding to 0.653 g. of levulinic acid. Calculated on the total amount (500 cc.) of Al solution, 13.06 g. of levulinic acid were obtained. The original 25 cc. required 0.3848 g. of NaOH for neutralization; the isolated levulinic acid corresponded to a consumption of 0.225 g. of NaOH. The volatile acids required 0.1275 g. NaOH, leaving 0.2573–0.225 g. NaOH for the non-volatile acids still present besides levulinic acid. This difference of 0.0323 g. of NaOH can be calculated either as acetic acid which was not driven off, or as succinic acid. In the first case there would be a yield of 0.97 g. for the total quantity of 500 cc., in the second, 0.95 g.

SUMMARY OF RESULTS FROM EXPERIMENT 5

20 G. of Total Rubber Were Used, or Based on the Carbon Skeleton, 17.65 G. (100%)

	Extraction of Levulinic Acid with Ether after Steam Distillation			The Same after Steam Distillation at Ordinary Pressure			Precipitation of Levulinic Acid after Previous Steam Distillation at Ordinary Pressure		
	Quantity, G.	Carbon Value, G.	Per Cent, C	Quantity, G.	Carbon Value, G.	Per Cent, C	Quantity, G.	Carbon Value, G.	Per Cent, C
Peroxide	6.675	3.040	17.23	6.675	3.040	17.23	6.675	3.040	17.23
Formic acid	0.806	0.211	1.19	0.864	0.225	1.28	0.864	0.225	1.28
Carbon dioxide	0.584	0.160	0.91	0.584	0.160	0.91	0.584	0.160	0.91
Levulinic aldehyde	4.189	2.520	14.28	4.189	2.520	14.28	4.189	2.520	14.28
Acetic acid	2.632	1.052	5.96	3.482	1.385	7.85	4.43	1.775	10.05
Levulinic acid	20.542	10.630	60.23*	18.822	9.736	55.34*	16.732	8.650	49.20
Succinic acid	0.218	0.087	0.50	Not detd.	Not detd.	Not detd.	Not detd.	Not detd.	Not detd.

* Here the levulinic acid was determined only by titration; the precipitation method was not used until later.

References

- ¹ Part XII preceding.
- ² "Untersuchungen," pp. 60, 62, 116.
- ³ Cf. the statements of Lecher, *Kautschuk*, **5**, 133 (1929), and Staudinger, *Ibid.*, 134.
- ⁴ Again with 1.5%. To remove alcohol, the chloroform was extd. with concentrated sulfuric acid and then with caustic soda solution, was dried, then distilled and kept under nitrogen.
- ⁵ Instead of zinc dust and acetic acid (cf. Harries and Haarmann, *Ber.*, **48**, 35 (1915); Helferich, *Ber.*, **52**, 1128 (1919)), because acetic acid may be a cleavage fragment.
- ⁶ Harries has already experimented with this reagent, but gave it up later because further reaction took place (cf. *Ber.*, **39**, 2850 (1906); *Ber.*, **48**, 35 (1915)).
- ⁷ See Part XII.
- ⁸ This reagent has been used for the detection of methylglyoxal and pyrrocemic acid by Neuberg (cf. Neuberg and Kobel, *Ber.*, **63**, 1986 (1930)).
- ⁹ Harries and Türk, *Ann.*, **374**, 338 (1910).
- ¹⁰ The first portion of the distillate gave the blue color reaction with sodium nitroprussiate, which indicates methylglyoxal, or as we found, pyrrocemic acid.
- ¹¹ Levulinic acid from rubber always reduces Fehling solution, and gives indigo with o-nitrobenzaldehyde, which might be explained by the presence of pyrrocemic acid. Like the latter and like methylglyoxal, these solutions also give with sodium nitroprussiate a blue coloration. See Neuberg, *Biochem.-Z.*, **71**, 155 (1916).
- ¹² *Ann.*, **292**, 249 (1896); Neuberg and Scheuer, *Ber.*, **63**, 3068 (1930). Detection of methylglyoxal by means of 1,2-naphthylendiamine. We have also used the same reagent in the detection of pyrrocemic acid.
- ¹³ Correction: Meantime it was found possible in a cleavage experiment with 20 g. of sol-rubber (Fraction II) to obtain 0.67% of the carbon skeleton in the form of acetaldehyde in the residual p-nitrophenylhydrazine solution.
- ¹⁴ For diagram see *Thesis*, K. Gerlach, Erlangen (1929).
- ¹⁵ Franzen and Greve, *J. Prakt. Chem.*, **80**, 386 (1909).
- ¹⁶ Wegner, *Z. Anal. Chem.*, **42**, 427 (1903).
- ¹⁷ An additional 0.264 g. of formic acid was condensed in a cooling coil beyond the receiver.

Rubber

Part XIV. The Behavior of Rubber with Iodine Chloride and with Dithiocyanogen

Rudolf Pummerer and Herman Stärk

UNIVERSITY OF ERLANGEN

1. The Determination of the Iodine Number of Rubber

The investigation of carotinoids has shown us that a large excess of iodine chloride must be employed if conjugated systems of double bonds are to be completely attacked.¹ If, for example, with isoprene 150% of the calculated quantity of iodine chloride is used, then the reaction reaches after one day and after one week only 1.77 and 1.80 double bonds, respectively. 200% of iodine chloride must be used in order to obtain the correct number of double bonds. A still greater excess of iodine chloride does not then change the results any further. Such isoprene systems, which have added a halogen atom on every carbon atom in the chain, are obviously stable to substitution by iodine chloride.

The frequently discussed question of whether in rubber a pair of conjugated double bonds is present as a terminal group, therefore a true isoprene system, has been proved by Pummerer and Mann² by means of iodine chloride. At that time, however, the results did not apply to isoprene. For that reason it was necessary again to titrate the rubber with a great excess of iodine chloride. In this way it was shown that trustworthy results were obtained only by using 110-120% of iodine chloride (100% = 1 mol. of iodine chloride per C_5H_8 group), accordingly with an excess of from 10-20% iodine chloride. Within this range the results of the titration did not vary. Also only very few (often none at all) acids appeared with the titration, and these could be disregarded. On the contrary, if a greater excess of iodine chloride is used, the iodine numbers and acid values are essentially higher, which, as is well known, indicate substitution. Thus with 200% iodine chloride a value of 147 was obtained. The same phenomenon is true of gutta-percha. The earlier titrations of rubber were accidentally carried out within the favorable range of excess iodine chloride, so that the values for sol-rubber have undergone scarcely any correction. We have now carried out iodine chloride titrations with six fractions of crepe sol-rubber extracted with cold acetone, then fractionally dissolved in cold ether, and in this way we have found, as for sol-rubber, values for alkali-purified latex. They are very close to 100 (Fraction I: 100.1; II: 100.3; III: 99.9, IV: 99.6; V: 100.0; VI: 99.9). No difference in the titre was established by the various fractions.

We now have found values for gel-rubber of 99.1, 89.3, and 99.1. Pummerer and Mann had already observed that the higher iodine numbers found by them of 108-110% were accompanied by the evolution of a hydrogen halide in the chloroform solution. If this hydrogen halide is subtracted on the basis that it is the result of substitution, then values for gel-rubber are obtained which also are close to 100%. It has now been established that this value can be directly obtained if no greater excess of iodine chloride is used than 20%. No fundamental difference between sol- and gel-rubber seems to be evident in any facility of substitution by iodine chloride.^{2a}

The method of iodine chloride determination has now been altered in the sense that, although we prepare the rubber solution now as before in chloroform under

nitrogen, the iodine chloride solution is, on the contrary, prepared in carbon tetrachloride, in which it is more stable. In this way less acid is formed than in chloroform. Were it desired to use carbon tetrachloride as solvent for rubber, the iodine chloride addition product of rubber would precipitate in part, whereby the reaction is made more difficult. The limit of error of the method of a single determination lies between $\pm 0.3\%$.

From the results of the determination of the iodine number of isoprene, in order to prove a terminal isoprene group as a conjugated system in rubber, a very great excess of iodine chloride (about 200% in all) would have to be used. Such an excess is not borne by the carbon skeleton of rubber without substitution. One cannot prove therefore by means of iodine chloride on this basis the presence of an isoprene group. Therefore the optical method (ultra-violet absorption) is unquestionably superior.

Experiments with unbranched chains (hentriacontene and cyclohexene) have shown us that here an excess of iodine chloride does no harm. For example, 0.1823 g. cyclohexene was used with 99.6% of iodine chloride with 50% excess, and a reaction time of $3\frac{1}{2}$ hours. No acid was formed. On the contrary, limonene behaves like rubber. Mann found the iodine chloride consumption corresponded to 2.0 $\bar{\text{I}}$, Reindel, on the other hand, found that it corresponded to 2.2 $\bar{\text{I}}$. Here, too, the reason for the difference lies in the different excess of reagent used. We have now found 99% of the theoretical iodine consumption for 2 $\bar{\text{I}}$, with 15–20% excess, while with 50% excess, 104% was found. Trimethylethylene behaves like limonene.

According to these experiments, it is surprising that the polyene chain of carotinoid is so resistant to great excess of iodine chloride, which obviously in this instance depends upon the especially heavy loading of the main chain with halogen. With carotin, as a result of the hydro-aromatic terminal groups, we have established a greater consumption, corresponding to about 0.3 $\bar{\text{I}}$.

TITRATIONS OF DIFFERENT RUBBERS IN CHCl_3 WITH IODINE CHLORIDE
(Dissolved in CCl_4)

Kind of Rubber	ICI Excess in Per Cent Based on $[\text{C}_5\text{H}_8]_n$	Reaction Time, Hours	ICI No. in Per Cent of the Theory	ICI No. Corrected after Deduction of Acid (Calculated on Substitution)
Latex, alkali purified	5	120	96.6	93.3
Sol-Rubber, Fraction II	20	5	99.9	98.0
	33	5	101.4	95.5
	20	6	100.2	98.3
Fraction VII	20	18	99.3	96.9
Gel-rubber	20	18	99.1	97.1
	20	5	99.1	96.3
	20	48	100.1	98.1
Total rubber	20	50	99.8	97.8
Sol-crepe rubber extracted with cold acetone and ether, Fraction I	20	5	100.1	98.0
Fraction II	20	5	100.3	98.3
Fraction III	20	6	99.9	97.9
Fraction IV	20	6	99.6	97.6
Fraction V	20	6	100.0	97.6
Fraction VI	20	6	99.9	97.5
Crude smoked sheets	20	6	95.9	91.3

The titrations were so carried out that about 0.1 g. rubber was dissolved at one time under purified nitrogen in 50 cc. CHCl_3 . To this solution was added a 0.2 N ICI solution, whose titre had been previously determined with a 0.05 N thiosulfate solution. Recalculated on a 0.05 N solution, 0.1 g. of rubber consumed theoretically 58.8 cc. ICI-solution to which must be added the excess.

A SERIES OF EXPERIMENTS. RUBBER TITRATIONS WITH ICI, DEPENDENT UPON AN EXCESS OF ICI

Kind of Rubber	ICI Excess in Per Cent, Based on $(C_5H_8)_n$	Reaction Time, Hours	ICI No. in Per Cent of the Theory	ICI No. Corrected after Deduction of Acid (Calculated on Substitution) in Per Cent
Latex, alkali-purified	2	6	92.8	89.6
Sol-rubber, Fraction II	2	23	93.9	90.6
	5	6	95.3	92.4
	5	15	95.6	..
	10	6	99.3	95.7
	10	23	99.5	95.2
	12	7	99.6	96.4
	15	23	100.2	94.8
	20	4	99.9	95.9
	20	5	100.1	95.4
	20	5	100.0	93.2
	20	24	100.4	95.7
	25	23	101.3	93.2*
	33	4	102.0	92.2
	33	5	101.8	93.6
	40	5	102.9	92.6*
	40	24	104.5	87.4
	52	5	105.3	96.4
	52	24	107.2	86.8
A similar preparation only 1/2 year older	10	29	98.6	No acid
	10	48	99.3	98.5
	12	52	99.3	98.3
	20	4	99.3	No acid
Crepe sol-rubber, Fraction II	214	24	148.8	92.8*
	190	22	142.3	96.7
Gutta-percha	85	6	113.6	79.6*
	85	50	117.6	70.7

* The values starred show plainly, especially in comparison with the acid-free values, that the uncorrected I nos. are conclusive. The acid certainly arises partly through cyclization also, as, for example, the value of 70.7 with gutta-percha shows, which is impossible according to the extinction coefficient.

To decide the problem whether the hydrogen halide, which is formed in rubber with a great excess of iodine chloride, arises from direct substitution, or whether hydrogen halide also can be split off with reformation of a double bond, which then required more iodine chloride, we have tested vinyl bromide by the iodine chloride addition reaction. It reacted essentially slower than an ordinary olefin, but finally with the use of 180% of iodine chloride complete saturation was reached after 50 hours. The symmetrical dichloroethylene on the contrary did not enter into the reaction at all.

In these experiments, the iodine chloride number was characterized by a well-defined constancy, which held true with an excess of about 10-20% iodine chloride. Within this range the value is independent of the time of the reaction and of the dilution, while in the higher range of an excess of about 40% iodine chloride, the substitution goes on progressively and so reaches no utilizable limiting value.

VINYL BROMIDE

With Ethylenes Having Dihalogens as Substituted Double Bonds, like Dichloroethylene, No ICI Is Added, Whereas the Monohalogen Substituted Ethylenes Took It Up Very Slowly, *i. e.*, Vinyl Bromide

ICI Excess in Per Cent	Reaction Time, Hours	ICI No.	ICI No. Corrected after Deduction of Acid
80	5	77.7	75.8
80	28	97.7	94.1
80	50	99.9	96.3

LIMONENE

ICI Excess in Per Cent	Reaction Time, Hours	ICI No.	ICI No. Corrected after Deduction of Acid
15	25	98.9	96.8
20	3	98.8	97.3
50	7	104.0	94.4
50	24	104.2	95.4

II. The Addition of Dithiocyanogen to Rubber

The thiocyanogenometric titration of double bonds developed by Kaufmann³ also seemed to offer promise of being used with rubber in order to determine whether particularly reactive double bonds enter into reaction quicker than others. For the complete reaction of a terminal isoprene group, thiocyanogen does not enter into the question, since isoprene itself forms⁴ only one dithiocyanide of the formula $C_5H_8(SCN)_2$, and therefore reacts with only one double bond toward the cyanogen, as it does toward perbenzoic acid.⁹ But apart from this we have found no advantage in the use of thiocyanogen in the place of iodine chloride, but only disadvantages which arise in part from the jelly-like character of the solution, as in cold vulcanization with sulfur chloride in solution.⁶ This made the removal of samples and the preparation of the thiocyanogens at the right moment very difficult. There was only a relatively short time interval in which a constant consumption of thiocyanogen took place, then there began, induced either by the rubber thiocyanide or through traces of liberated HSCN, a gradual decomposition of the excess thiocyanogen.

Nevertheless we were able in a series of experiments, where each experiment was carried out five to ten minutes after the preceding one, to ascertain in the time interval during which the consumption of thiocyanogen was constant, a consumption of thiocyanogen which corresponded to the addition of 1 molecule of dithiocyanogen per C_5H_8 . The values lay between 96 and 100% of the theoretical thiocyanogen number, both for sol- and for gel-rubber, and when represented graphically were manifest as a horizontal section of the curve, with the time as abscissa and the theoretical per cent of the added thiocyanogen as ordinate. The constancy was found only at a working temperature of 0° , and lasted only ten to twenty-five minutes, after which decomposition of the free thiocyanogen began. The increase to the constant range lasted thirty to sixty minutes, in dried carbon tetrachloride (under CO_2), and one to two days in chloroform. Accordingly the work was always done in carbon tetrachloride.

Analytically pure rubber thiocyanide could not always be isolated, even when the reaction was interrupted at the right time, so we can give no reliable directions. The sulfur and nitrogen content lay mostly in the vicinity of the expected values, but during the process oxygen entered easily. The excess admixed polymeric thiocyanogen can be removed by extraction by warm acetone in a Soxhlet apparatus. We have obtained good analyses with such preparations.

The Preparation of Rubber Thiocyanide and the Practical Operation of the Thiocyanogen Titration.—To a 1% rubber solution in $CHCl_3$ or CCl_4 a 1 N or 0.5 N dithiocyanogen solution with an excess of about 50–100% was added, and made to react at 0° with exclusion of oxygen and light. After the reaction was ended, which was evident by a slight turbidity of the reaction mixture and by the appearance of syneresis, the reaction product was freed of solvent, after thorough washing with ether *in vacuo*.

0.1293 g. substance: 0.2133 g. CO_2 , 0.5236 g. H_2O . 0.1163 g. substance: 15.2 cc. N (15° , 744 mm.). 0.1062 g. substance: 0.2720 g. BaSO_4 .
 $\text{C}_6\text{H}_8(\text{SCN})_2$: Calcd., C 45.61, H 4.36, N 15.20, S 34.83; found, C 44.99, H 4.53, N 15.26, S 35.18.

Another product, which after its formation showed too high S and N content, gave the following values after acetone extraction:

0.1092 g. substance: 14.7 cc. N (18° , 746 mm.). 0.1147 g. substance: 0.2773 g. BaSO_4 . Found, N 15.51, S 33.20.

In the titration of rubber with free thiocyanogen, individual samples were tested under identical conditions, and after various periods of time the remaining free thiocyanogen of the individual samples was titrated back, and the titre calculated according to the consumption.

Thus a sol-rubber Fraction III from alkaline-purified latex gave the following values: After 55, 65, 70, 75, 86, 92 min., the consumption of thiocyanogen was 86.9, 98.0, 98.1, 98.4, 99.6, 103.3%, from which it can be seen that from 65–75 min. it was fairly constant.

Details of the results are to be found in the thesis by H. Stärk (Erlangen, 1930).

The work was carried out with the support of the Notgemeinschaft of the Deutschen Wissenschaften, to which we extend our best thanks.

References

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- ² *Ber.*, **62**, 2636 (1929). The method was first used with rubber by Fisher and Gray, *Ind. Eng. Chem.*, **18**, 414 (1926).
- ³ A. Gorgas (*Kautschuk*, **4**, 253 (1928) and *Ber.*, **63**, 2701 (1931)) used iodine bromide and obtained other results; however, a greater consumption of halogens always occurs if the reaction is allowed to continue longer than directed.
- ⁴ Kaufmann and Gärtner, *Ber.*, **57**, 928 (1924).
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- ⁶ Pummerer and Reindel, *Ber.*, **62**, 1415 (1929).
- ⁷ LeBlanc and Kröger have protected by *German Patent* 408,306, K. 39b (*Chem. Zentr.*, **1925**, I. 2596) a process for cold vulcanization with thiocyanates.

The Effect of Grit upon the Stress and Strain Properties of a Carbon Black Stock

E. P. W. Kearsley and C. R. Park

UNITED CARBON COMPANY, CHARLESTON, W. VA.

Numerous papers have appeared from time to time dealing with the detection of grit in rubber pigments, in practically all of which it has been tacitly assumed that grit seriously impairs the quality of the pigment. Rubber articles, especially tire treads, made with pigments containing even small proportions of gritty material are considered inferior, and specifications covering grit are usually quite rigid. Pigment manufacturers have gone to great lengths to produce grit-free pigments, and the resulting product undoubtedly justifies the additional manufacturing care exercised.

The importance of differentiating between actual grit and agglomerates of pigment particles which are subsequently dispersed during mixing operations has been pointed out by Murphy (*Trans. Inst. Rubber Industry*, 2, 100 (1926)), and various methods of accurately determining true grit have been suggested by this same author, by Gallie and Porritt (*Trans. Inst. Rubber Industry*, 2, 116 (1926)); by Esch (*Gummi-Ztg.*, 41, 82 (1926)), by Evers (*Kautschuk*, 1927, 70) and by others. The difficulty with which carbon black may be elutriated has limited the employment of such an agency in determining the proportion of grit present in it, and the laboratory has been confined to the use of screens of various size apertures for this purpose.

That the presence of small proportions of relatively coarse particles in carbon black may not impair the abrasion-resistance of rubber compounds employing it has been demonstrated by Twiss (*Trans. Inst. Rubber Industry* 2, 82 (1926)), who determined the abrasion-resistance of three mixings containing rubber and carbon blacks (identical with the exception of grit content) in the proportion of 100 : 40 as follows:

	Grit (90 Mesh Screen)	Abrasion Resistance
A	0	1.03
B	0.09	1.06
C	0.10	1.00

The explanation offered is that no simple relationship exists between resilient energy and abrasion resistance, which is further indicated by the disproportionate effects on these two characteristics produced by the introduction of an organic accelerator.

It is probable, especially in view of the above evidence, that particles of grit present in a tire tread stock are simply dislodged during the abrasion process and have no influence whatever upon the wear-resisting properties of the main body of the stock. The dislodgment of quantities of the order of 0.1% would certainly not produce a measurable effect.

It seems more logical to search for an effect of gritty material upon the tensile strength. The formation of vacua (cf. Green, *Ind. Eng. Chem.*, 13, 1029; Endres, *Ibid.*, 16, 1148), or the shearing action of sharp edges, are commonly considered causes of reduced tensile strength.

A reduction in tensile due to these causes seems not improbable in the case of the coarse and irregularly shaped particles in question. The literature offers little direct evidence upon the effect of grit in rubber mixes, and the present series of experiments has been conducted to fill this gap in our information.

A standard sample of carbon black was chosen, which gave practically no residue on a screen of one hundred mesh. Grit screened from carbon black at a carbon black plant was ground in a mortar until it passed one hundred mesh. Thus the maximum particle size was of the order of 100μ , and ranged down to considerably

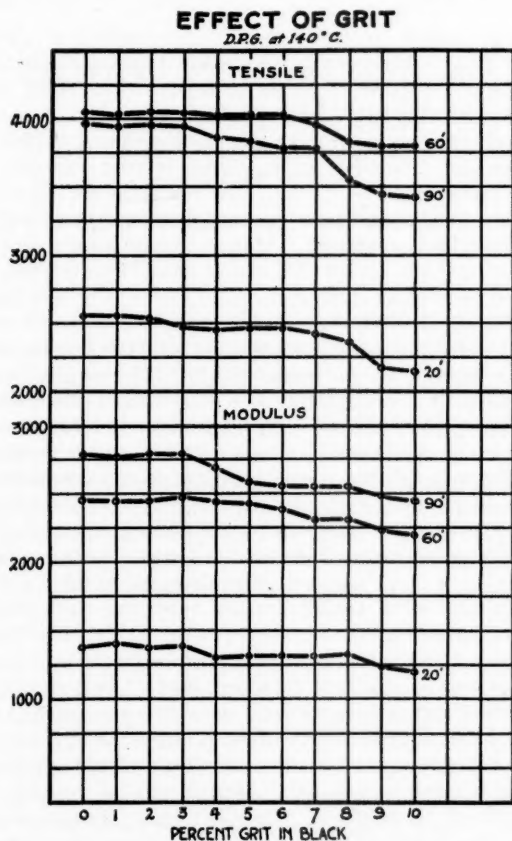


Figure 1

smaller dimensions. It can be taken for granted, however, that all the material was exceedingly coarse compared with channel black, which ranges in particle size from 40 to 120μ , according to various investigators. The material prepared as outlined above was added to the standard black in amounts to give a series of samples containing from 0 to 10% added grit. The resulting samples of black were mixed into rubber in the usual way, and tested for tensile properties.

In order to insure complete dispersion, the black was mixed into a 40 black: 60 rubber, master batch in all cases, and subsequently milled into the final stock.

The formula used as follows:

Rubber.....	100	Sulfur.....	3.50
ZnO.....	5	D. P. G.....	1.25
Carbon Black.....			47

Cures were made at 20, 60, and 90 minutes at 140° C.

Tests were conducted according to the recommended procedure of the Physical Testing Committee, except in the following respects: Surface speed ratios on the mill were 1 : 1.25, and tensile tests were made on the Goodyear type testing machine.

The results are shown in Figure 1. It is a rather astonishing fact that grit in quantities up to 3% has no measurable effect upon the tensile strength or modulus of the stock.

It is of course impossible to justify excessive proportions of coarse material in a pigment. These data do, however, make it evident that grit is by no means as objectionable as common opinion indicates in regard to its effect upon the stress-strain curve, and particularly the tensile strength.

When poor results are obtained from gas black mixes, it is probable that other factors are responsible. Notable among these is poor pigment dispersion. It has been pointed out by Endres (*loc. cit.*) that pigments are often in the rubber in an unwet condition, existing as large masses. These break up and form points of weakness when the rubber is stressed. Many precipitated pigments are difficult to wet and to disperse properly in rubber, and give tensile results which are lower than might be expected from their state of division. Lithopone is a notable case, and whiting and iron oxide are also offenders.

Due to the immense amount of surface to be wet, the problem of complete dispersion of carbon black is by no means simple. The emphasis which has been placed upon efficiency in American rubber factories has so reduced the time available for mixing that perfect or even good dispersions have become more and more difficult for the factory operatives to obtain. It is probable that premature tread wear and tread cracking are frequently attributable to over-emphasis of the time consumed in the mixing operation and under-emphasis of the results obtained.

With these facts in mind, it seems that tests concerning the degree of dispersion obtained in the mix would be more effective in insuring quality than tests directed toward the detection of small proportions of coarse material.

Some Properties of Carbon Black

I—Adsorption¹

W. B. Wiegand and J. W. Snyder

BINNEY & SMITH CO., 41 EAST 42ND ST., NEW YORK, N. Y.

The diphenylguanidine (D. P. G.) adsorption test correlates well (0.8) with rubber-curing behavior in organically accelerated mixings, in respect to the broad classes of carbon black, but only moderately (0.4) in respect to standard rubber carbon black. The D. P. G. or similar adsorption test, although correlating better than the volatile-matter test, is therefore not capable of predicting with precision the rubber-compounding behavior of standard (rubber) carbon black.

Carbon-black adsorption is much more marked in the alkaline than in the acid range.

While heat-activated carbon blacks show marked increase in D. P. G. adsorption, heat-deactivated carbon blacks show greatly reduced alkaline and slightly increased acid adsorption,² which probably explains the anomalous iodine adsorption of heated blacks noted in the literature.

In litharge compounds without added fatty acid, high-adsorption blacks spoil the cure by removing the fatty acid present in the rubber. Heat-deactivated carbon black leaves the cure relatively unaffected. In litharge compounds containing an excess of added fatty acid, however, both heat-deactivated and high-adsorption blacks improve the cure, doubtless through removal of excess acid. In general, for carbon black-litharge compounds a low-adsorption carbon black is preferable because it permits a minimum dosage of fatty acid.

For entirely unaccelerated rubber mixings heat-deacti-

¹ Received April 6, 1931. Presented before the Division of Rubber Chemistry at the 81st Meeting of the American Chemical Society, Indianapolis, Ind., March 30 to April 3, 1931.

² True for aqueous and alcoholic hydrochloric and benzoic acids.

vated (low-adsorption) carbon black exhibits striking improvement in physical properties.

The adsorptive properties of carbon blacks have been turned to advantage in the fields of rubber insulation and insulating oils. High-adsorption, heat-activated carbon blacks are shown to advance the cure of rubber mixings vulcanized with *m*-dinitrobenzene. Specially activated carbon blacks have been developed which show a higher (alkaline) adsorptive effect than the active chars now on the market. It has been found possible to produce new grades of carbon black in which both the magnitude and direction of adsorptive activity are under control.

IN 1925 Le Blanc, Kroger, and Kloz (8) reported that they could find no relation between the properties in rubber and the adsorptive properties of lampblack. The latter, when suspended in an organic medium, showed no adsorptive capacity for sulfur, iodine, or mercaptans.

Later in the same year Thies (12) showed that with clays there was a relation between the adsorption of basic dyes (malachite green) and rate of cure. The lower the adsorption of dye the faster was the rate of cure. On the other hand, it was shown that with some acid dyes the faster curing clays had a greater dye adsorption. This difference in the rate of cure of the clays, however, was apparent only in organically accelerated rubber compounds.

In 1926 Twiss and Murphy (13) came to the conclusion that the retardation in cure of an unaccelerated mixing, by carbon black, was attributable to the adsorption of the natural accelerator in the rubber.

Spear and Moore (10) found no relation between the stiffening power of carbon blacks in rubber and the adsorption of malachite green from aqueous solutions, Victoria blue from benzene, and hexamethylenetetramine from benzene. However, they found some evidence that differences in adsorption of hexa ran parallel with differences in time of cure.

In 1928 Goodwin and Park (3, 6) showed clearly that high-color paint blacks, rubber blacks, and certain thermal-decomposition blacks gave different adsorption isotherms towards iodine and methylene blue solutions in water and carbon tetrachloride. They concluded that adsorption differences exert a profound influence upon the properties in rubber.

Beaver and Keller (1) concluded that the rate of cure was not related to the adsorptive behavior.

In 1929 Carson and Sebrell (2) showed in a very stimulating paper that, except for blacks that had been heat-treated, the adsorption behavior toward benzoic acid, iodine, mercapto, and diphenylguanidine was a measure of the rate of cure.

Wiegand (14) employed the adsorption of diphenylguanidine in alcohol and of potassium hydroxide in water to illustrate the reduced activity and enhanced curing properties of some new carbon blacks.

Johnson (7) reported no correlation between iodine adsorption and rate of cure, except in samples coming from the same factory. He found positive correlation between volatile content and the adsorption of two organic accelerators, Captax and diphenylguanidine. He also confirmed the "exception" already noted by Carson and Sebrell—viz., that heated blacks showed decreased volatile together with increased iodine adsorption.

Fromandi (5) determined the adsorptive isotherms of various blacks for acetic acid, but has thus far offered no correlation with rubber properties.

Ditmar and Preusse (4) used methylene blue in aqueous

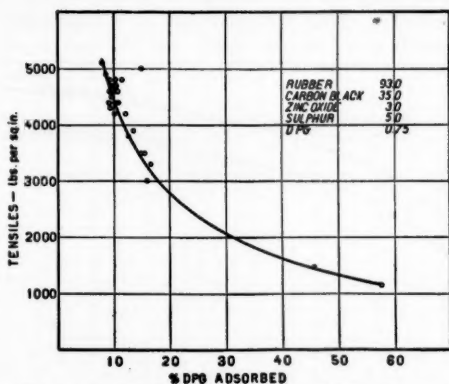


Figure 1—Diphenylguanidine Adsorption vs. Tensiles of Rubber, Paint, and Ink Carbon Blacks in Accelerated Rubber Compound

solution. They state that the retardation of cure by carbon black is due solely to removal of sulfur.

A glance over the published work on adsorption as a clue to the vulcanizing behavior of carbon blacks at once invites the conclusion that there is some intimate relationship between these two properties. The adsorption of Captax, diphenylguanidine (D. P. G.), and potassium hydroxide has, for example, been stated to run parallel to volatile or to rubber-curing behavior. On the other hand, important exceptions have been noted; the iodine adsorption, especially for heated blacks, seems to have given anomalous results.

In this paper an attempt has been made to assess the validity of the adsorption test and to resolve some of its apparent anomalies.

Adsorption as a Quality Test

THE TEST—In order to fix ideas, the test as worked out in these laboratories is given. Two grams of C. P. di-

phenylguanidine are dissolved in 1 liter of ethyl alcohol U. (S. denatured formula No. 1 has been successfully used), and 50 cc. of this solution are shaken with 1 gram of the sample for 2 hours. After filtering, 25 cc. of the filtrate are titrated with 0.01 *N* hydrochloric acid using a mixture of bromophenol blue and methyl red. The result is expressed as the percentage of D. P. G. removed.

ACCURACY—A review of many duplicate tests shows a mean deviation of well under 5 per cent. This indicates a probable error distinctly lower than the variability due to differences in quality. In other words, the test is satisfactory as regards chemical accuracy.

CORRELATION WITH RUBBER PROPERTIES—Figure 1 shows the relation between the D. P. G. test and the tensile strength of rubber stocks developed after 30 minutes' cure at 40 pounds (2.7 atm.) steam pressure in a laboratory press. The test formula is shown on the graph and the blacks tested included "Super" quality rubber black (de-oxygenated), stand-

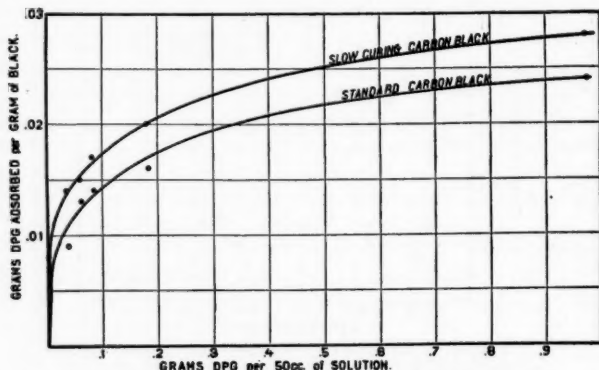


Figure 2—Adsorption Isotherms. Rubber Carbon Blacks in Alcoholic Solutions of Diphenylguanidine

ard rubber black, Class 11 rubber black, paint black, and ink black.

The curve represents thirty-five pairs of determinations and is broadly hyperbolic. As such it is not suitable for statistical treatment by Pearson's methods, for the coefficient of correlation requires a linear disposition. However, by omitting the two very high values for adsorption—which, in fact, belong to paint and ink blacks which are never used in rubber—the remaining data approximate a straight-line relationship and so are amenable to the calculation of Pearson's coefficient.

This value is, in fact, -0.8 ± 0.04 . Since a coefficient of 0.5 is commonly held to constitute definite correlation and since the probable error (0.04) is only one-twentieth of the coefficient, it is manifest that, speaking generally, there is a very direct connection between the behavior of the black in a rubber compound accelerated with D. P. G.

and the capacity of the black to remove D. P. G. from its alcoholic solution.

The total breakdown of this correlation when the rubber compound is inorganically accelerated will later be illustrated in detail.

TEST APPLIED TO STANDARD (RUBBER) CARBON BLACK—For this series a set of one hundred control tests was taken at random from the laboratory records. The samples were taken from various channel plants of similar construction and producing the same grade of carbon black. The black was of standard rubber quality (Micronex). In the interest of increased accuracy the tensile at break was replaced by a weighted modulus as follows: In the standard test formula (vs) the stress at 300 and at 500 per cent was averaged for both a 30-minute and a 40-minute cure. Thus in effect the rate-of-cure index was the average of four modulus values (approximately equal to modulus at 400 per cent for 35-minute cure). The D. P. G. adsorption test was carried out as described above. The results have been thrown into a frequency table (Table I).

Table I—D. P. G. Adsorption vs. Mean Modulus in Accelerated Rubber Mixing, Using Standard (Rubber) Carbon Black

D. P. G. TEST %	MEAN MODULUS IN RUBBER							
	<1699	1700- 1749	1750- 1799	1800- 1849	1850- 1899	1900- 1949	1950- 1999	2000- 2049
> 12.0	2	1	-	-	-	-	-	-
11.5 to 11.9	-	1	1	-	-	-	-	-
11.0 to 11.4	1	1	-	2	-	1	-	-
10.5 to 10.9	2	-	-	1	-	1	-	1
10.0 to 10.4	-	-	1	2	5	-	2	-
9.5 to 9.9	2	1	-	4	5	2	1	-
9.0 to 9.4	1	-	5	3	6	4	-	2
8.5 to 8.9	-	1	2	4	7	3	6	3
8.0 to 8.4	-	-	-	1	1	4	3	-
7.5 to 7.9	-	-	2	-	1	1	-	-

Casual inspection of Table I will show the presence of correlation, but at the same time a marked degree of dispersion, for perfect correlation would require all the data to be concentrated along one of the diagonals of the table.

The correlation coefficient for the above set of one hundred determinations was -0.46 ± 0.05 . This value may be regarded as indicating definite correlation, the degree of which, however, is much inferior, for example, to the value (-0.8) obtained over the wider spread of carbon-black qualities.

These correlation values for the D. P. G. adsorption test as compared with the rubber-compounding and -curing properties led to the conclusion that this test may with advantage be included in any examination of a new sample of carbon black in order to obtain a preliminary idea of its curing characteristics in organically accelerated tread-type rubber compounds; that the test is quick, inexpensive, and of sufficient manipulative accuracy; but that, in its present form, it is not capable of predicting with precision the rubber-compounding behavior of successive samples of standard carbon black.

Comparison with Volatile Test

The volatile test has also been proposed as a quality test for rubber carbon black, and it is hoped to discuss this test in detail in another place. For the present it will suffice to state that, for the same group of test data as is shown in Table I, the coefficient is -0.24 ± 0.06 , a value well below the lower limit for correlation.

Adsorption Isotherm for Alcoholic D. P. G.

Figure 2 shows two isotherms, that of a standard (rubber) carbon black and that of a slower curing grade. The proportions of black and D. P. G. adopted for the standard procedure correspond to approximately 0.1 on the abscissa. Higher concentrations would involve lower percentages of D. P. G. removal; lower concentrations would lead to titration difficulties.

Selective Character of Carbon-Black Adsorption

Carbon black usually assumes a negative charge when suspended in liquids. It is therefore peptized by negative ions and so would be expected to exhibit selective adsorptive effects toward such negative ions. That such is in fact the case is illustrated in Figure 3, in which are shown the molar adsorptions for standard (rubber) carbon black on both sides of the neutral point.

The marked asymmetry of the curves for acid and alkaline adsorption is an important characteristic, a clear conception of which was an essential step in the development of the newer grades of carbon black (14).

Adsorption Characteristics of Heated Blacks

Blacks heated in the presence of air or steam become more active (9, 11). Blacks so treated will be designated as "activated." The extent of such activation is shown in Table II.

Table II—Effect of Activation on D. P. G. Adsorption of Carbon Blacks

CARBON BLACK	Before activating	After activating
	%	%
Standard rubber	11.4	30.5
Standard paint	40.0	93.0
Standard ink	58.0	64.0

Blacks heated in the absence of air have been found to show at the same time a decreased volatile content and an increased adsorption of iodine. This peculiarity was noted by Sebrell and Carson and later by Johnson. This type of black will be hereafter designated as "deactivated."

Figure 4 shows the change in selective adsorption of carbon black deactivated by heat treatment in the absence of air. The alkaline adsorption is seen to have been cut in two, but the acid adsorption has been increased. In other words, the effect of the heat treatment has been to alter the character

of the surface in such a way as to correct the asymmetry of the adsorption as regards basic and acidic substances. Herein, the writers think, lies the explanation of the anomalous iodine adsorption noted above.

The circumstance that the proper vulcanization of rubber takes place only in an alkaline medium offered a unique opportunity to capitalize this altered adsorption balance. The newer carbon blacks may therefore be described as having a corrected adsorptive tendency, the excessive distortion towards alkaline adsorption having been eliminated.

Adsorption in Litharge Mixings

The totally different picture presented when high- and low-adsorptive blacks are compounded in litharge mixings is shown in Table III.

Table III—Adsorption Properties in a Litharge Compound with and without Added Fatty Acid

D. P. G. CURE AT ADSORPTION 40 LBS.		WITHOUT ADDED FATTY ACID			6% STEARIC ACID ADDED		
		L-300 Tensile lbs./sq. in.	Elong. %		L-300 Tensile lbs./sq. in.	Elong. %	
STANDARD CARBON BLACK							
11.4	10	1150	4100	600	625	3900	710
	20	1450	4200	550	925	4400	680
	30	1700	4100	520	1350	4500	610
	40	1800	3800	470	1550	4600	560
	60	1950	3600	440	1850	4300	520
HEAT-DEACTIVATED CARBON BLACK							
8.0	10	1100	4000	610	675	3900	705
	20	1450	4300	570	1100	4600	660
	30	1700	4300	550	1400	4500	580
	40	1750	4000	505	1550	4500	580
	60	1900	3100	400	1900	4300	520
PAINT BLACK							
40.0	10	1250	3500	550	450	3900	750
	20	1400	3400	510	925	4700	680
	30	1500	3100	460	1350	4800	610
	40	1500	2800	430	1450	4600	570
	60	1550	2600	415	1500	4300	550
HEAT-ACTIVATED PAINT BLACK							
75.0	10	1800	3000	410	1550	4200	550
	20	1900	2600	370	2450	4300	460
	30	2000	2700	365	2400	4200	425
	40	2000	2400	330	2300	3900	425
	60	2000	2200	320	2250	3400	380

In those cases where the only available fatty acid was that present in the rubber, the high-adsorption blacks spoiled the cure just as they do in organically accelerated mixings except that the mechanism is, of course, removal of natural fatty acid. The heat-deactivated black did not remove enough acid to disturb the cure. In the experiments with the mixing to which 6 per cent stearic acid has been added, the cure has been definitely improved both by the heat-deactivated (low-adsorption) and the high-adsorption color blacks. In fact, the best cure of all was with the heat-activated paint black having a D. P. G. adsorption value of 75 per cent. The explanation seems to be that the blacks removed, in varying degrees, the excess of fatty acid present. A similar series with 10 per cent stearic acid showed the same general phenomenon.

The conclusion seems warranted that in litharge mixings there is only one content of fatty acid which will give the best curing results. This value depends, of course, on the percentage of litharge present.

The addition of carbon black will in general disturb this fatty acid equilibrium, so that the effect upon the cure of the addition of, say, 25 volumes of black will depend upon both the dosage of fatty acid and the adsorption activity of the black. Thus, there is only one proper fatty acid dosage for each grade of carbon black, and conversely, if the acid dosage

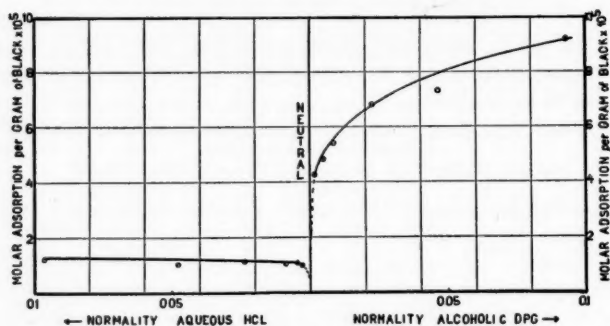


Figure 3—Standard (rubber) carbon black

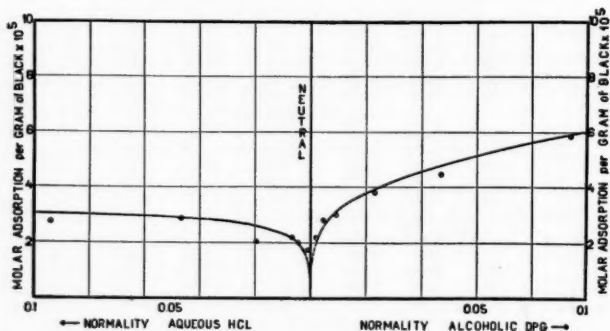


Figure 4—Special heat-treated carbon black

Selective Adsorption Isotherms. Acid (HCl) vs. Alkali (D. P. G.)

is fixed, a black of suitable adsorption must be chosen in order to get the best cures.

Since excessive additions of fatty acid are not practicable for present-day litharge compounds (footwear, etc.), it would seem from the above data that a carbon black of low adsorptive activity should prove most satisfactory. In fact, the newer deactivated, low-adsorptive carbon blacks have already found application in this field of compounding.

Low-Adsorptive Blacks in Unaccelerated Mixings

The striking improvement in curing behavior shown in Table IV may be ascribed to the non-adsorptive blacks' not

having removed the natural accelerators present in the crude rubber.

Table IV—Curing Data on Low-Adsorptive Blacks in Unaccelerated Mixings

(Rubber, 93; carbon black, 35; zinc oxide, 3; and sulfur, 5. Cure, 120 minutes at 40 pounds)

CARBON BLACK	TENSILE <i>Lbs./sq. in.</i>	ELONGATION %	T. P.	D. P. G. ADSORPTION %
Standard (rubber)	2200	580	128	11.4
Heat-deactivated	3600	590	212	5.1

Carbon-Black Adsorption and Electrical Insulation

It has recently been shown that the "removal" activity of carbon black may be turned to advantage in rubber insulation for wires, etc. (15), and also in the improvement of insulating oils (16). The very property which is so damaging in modern organic rubber compounds is capable of increasing by one-half the electrical insulating properties of these substances.

Low- and High-Adsorptive Blacks in Nitrobenzene Mixings

The tests reported in Table V were made in the belief that if, as some think, the nitrobenzene cure is an "oxygen" cure, the paint black, which has an oxygen content of about 7.0 per cent, might behave differently. These data, which are fully confirmed by hand tear tests, indicate that the highly adsorptive black, which in an organically accelerated sulfur mixing would have been difficult, if not impossible, to cure no matter how long prolonged the heating, was in fact badly overcured in 30 minutes.

Table V—Curing Data on Blacks in Nitrobenzene Mixings

(Pale crepe, 100.0; carbon black, 30.0; litharge, 9.5; and *m*-dinitrobenzene, 3.0 parts)

BLACK	D. P. G. ADSORPTION %	CURE		TENSILE <i>Lbs./sq. in.</i>	ELONGATION %	T. P.
		AT 40 LBS. <i>Min.</i>	L-300			
Standard (rubber) carbon	11.4	30	625	3600	690	248
		40	675	4000	680	272
Heat-deactivated rubber	8.0	30	700	3600	680	245
		40	825	3900	650	253
Paint	75.0	30	1250	3150	500	155
		40	1450	3300	480	158

The interpretation, practical as well as theoretical, of this result we leave to those who are proficient in this esoteric phase of rubber technology!

Comparison with Active Chars, etc.

The adsorptive activity of carbon black having at last yielded, in considerable measure, to artificial control, it may be of interest to compare its activity with that of the older forms of adsorptive or active carbon.

In general, it will be noted that the (alkaline) adsorptive activity of carbon black may be controlled between the widest limits, surpassing in this respect even the most active

chars. In acid adsorption, however, the carbon blacks show a range of from 0 to only 12 per cent.

Table VI—Comparison of Adsorption Activity of Carbon Black with That of Other Forms of Active Carbon

BLACK	HCl REMOVED	D. P. G. REMOVED
	%	%
Heat-deactivated carbon	7	8
Standard rubber carbon	3	12
Paint	12	40
Ink black	0	57
Darco	32	57
Suchar	70	71
Activated paint	11	80
Merck blood charcoal	54	95
Super-activated carbon	5	96

It is suggested that these newly developed adsorptive properties may find application in the arts of decolorizing, deodorizing, etc. The specificity of such "removal" effects is noteworthy and seems to be unapproached by other forms of carbon.

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Effect of Storage on Milled Crude Rubber¹

C. M. Carson

THE GOODYEAR TIRE & RUBBER COMPANY, AKRON, OHIO

Smoked sheets which have been milled to different degrees of plasticity and stored in bale form for periods up to 9 months show a decided increase in modulus, plasticity, and recovery values. The increase in recovery value is the most noticeable, the change being 180 per cent of the original, if the rubber is baled at 40–50° C. and stored at 10–20° C. for 9 months.

When the aged, milled rubber is mixed in a tube stock and processed on a tubing machine, the stock is rougher and the speed of extrusion is slower than a similar stock containing freshly milled crude rubber. The plasticity of stocks which are subjected to tubing operations is shown best on an extrusion type plastometer in preference to the compression type.

Milled crude rubber "freezes" at temperatures below 0° C. and thaws at room temperature of 15–25° C. It may be permanently frozen by being placed under slight pressure for several months, freezing temperature being unnecessary. In either sheet or milled form this type of frozen rubber requires a temperature of about 50° C. to thaw, whereas temporarily frozen rubber will thaw at room temperature.

OUR knowledge of cured rubber, aged for various periods of time is fairly extensive. The fact that uncured rubber also undergoes certain changes, even over short storage periods ranging from a few hours to several days, is also known in a general way. It was considered interesting to study the effect of longer aging periods along this same line.

¹ Received March 16, 1931. Presented before the meeting of the Akron Rubber Group of the American Chemical Society, February 19, 1931.

When plasticized or so-called broken-down rubber is not used within a reasonable period, it regains a certain amount of "nerve" and becomes more difficult to handle in ordinary factory processes. This paper deals primarily with the effect of storage at different temperatures on milled crude rubber, in an attempt to translate the general term "nerve" into definite physical properties such as plasticity, modulus, and rate of cure. This investigation was conducted on a factory scale in order to permit comparisons between typical factory operations and these physical properties, and a total amount of 40,000 pounds of rubber was used.

The literature contains a number of articles dealing with changes taking place in rubber at certain definite temperatures. Among these is an article by Griffiths (1) appearing in 1926, in which he evaluated "nerve" in terms of extrusion plasticity. He showed that the plasticity figure did not increase for periods up to 30 hours after the rubber had been cooled below 55° C. He did not continue his experiment beyond 30 hours, and it is this longer period extending into months which the present paper attempts to cover.

Experimental Methods

Smoked sheets were milled under definite procedures to produce four different plasticity grades ranging from slightly to thoroughly plasticized rubber, and stored at two temperatures (10–20° C.) and at 55° C., for periods up to 9 months. For convenience in handling, the rubber was baled, 225 pounds per bale, using pressures of 60 to 70 pounds per square inch to exclude air; and in order not to overlook any effect of original temperature, the bales were prepared with rubber at three temperatures—43°, 72°, and 100° C.

Plasticity values are based on the Williams plastometer under the following testing conditions: a 1-cc. pellet, under 10 kg. pressure for 3 minutes at 70° C., the compressed height being expressed in millimeters times 100. The regain or recovery value is based on a 1-minute recovery expressed in the same way. The four plasticity groupings used in this work were 390, 350, 325, and 275. The first was obtained by one breakdown on an 84-inch mill, the second by one breakdown on a 60-inch mill set at a somewhat tighter gage, the third by remilling 390 rubber, and the fourth by remilling 325 rubber.

Results

The effect of storage is most noticeable in the recovery value with but slight change in the plasticity figure, except for the longest storage periods. The recovery value increases consistently under all conditions investigated up to 9 months, the greatest increase being with 275 plasticity rubber baled at 43° C., and stored at room temperature (10–20° C.). This increase is about 180 per cent of the original recovery

figure. The least increase, 80 per cent, occurred with 390 rubber baled at 100°C . and stored at 55°C .

The modulus of the rubber showed a decided increase similar to that noted in recovery. However, modulus was increased most by storage at 55°C ., whereas the plasticity and recovery figures had been increased most by storage at room temperature.

The change in rate of cure was usually one of gradual, but slight, increase; i. e., the best cure changed from 40 minutes at 126.5° to 35 minutes at 126.5°C .

Figure 1 is a cooling curve showing the time required by rubber, baled at different temperatures, to come to equilib-

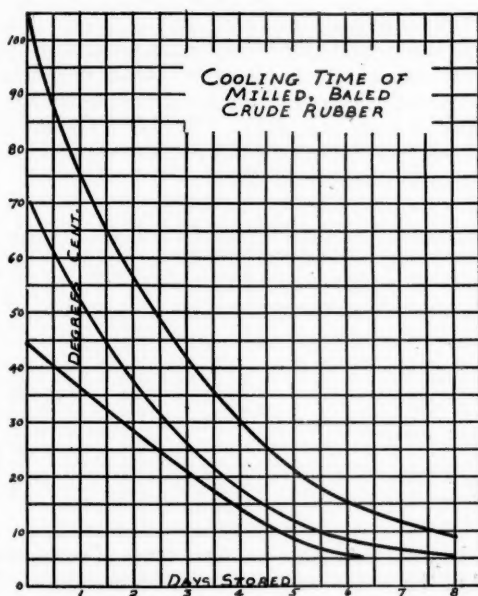


Figure 1

rium. Measurements were made by thermocouples inserted in the rubber at the time the bales were prepared.

The increase in physical property values is shown in Figures 2 to 5.

Figure 2 shows the percentage increase in recovery due to storage temperature. The recovery value is used in preference to the plasticity increase, since it was found to be a more definite and uniform figure. Storage at room temperature of $10\text{--}20^{\circ}\text{C}$. was found to give a gradually increasing recovery value, ending at 130 per cent in 9 months. Storage at 55°C . caused a smaller increase of 110 per cent in 9 months.

The effect of baling temperature is shown in Figure 3. Rubber baled at 43°C . increased in recovery to a figure 180

per cent higher than the original, in 9 months, while rubber baled at 100° C. showed a much smaller increase.

Figure 4 shows the effect of the original plasticity groupings in which the rubber had been divided. In this case the increase in plasticity value was plotted. As would be expected, the softest rubber showed the greatest increase, while the rubber which had been worked the least showed the smallest change. In general, the average plasticity increase was sufficient to place the rubber in the next higher plasticity group. Table I shows the percentage increase in plasticity.

The modulus changes were of a somewhat different nature. All samples were cured in the following formula: rubber 100, zinc oxide 4, sulfur 6, and captax 0.5.

The cure was 40 minutes at 126.5° C., the modulus being taken at 700 per cent elongation on the Goodyear autographic machine. The most marked effect is the increase in modulus shown by storage at 55° C. (Figure 5). Up to 6 months there was a consistent increase in modulus of samples stored either at room temperature or at 55° C. The last 3 months showed a still further increase in modulus of bales stored at 55° C., but not in those stored at 10-20° C.

Table I—Increase in Plasticity Values Due to Different Original and Storage Conditions

	3 MONTHS	6 MONTHS	9 MONTHS
	%	%	%
Temperature stored:			
10-20° C.	6.8	6.1	13.7
55-60° C.	6.6	7.9	10.5
Temperature baled:			
40-45° C.	6.4	6.8	10.7
70-75° C.	7.6	7.3	12.1
Over 100° C.	4.9	6.6	8.3
Original plasticity:			
275	7.1	8.6	12.9
325	7.4	7.7	11.9
350	5.5	5.5	9.8
390	5.9	5.5	8.3

It was impossible to get a complete range of cures on every sample, but this was obtained on every tenth sample. These results, taken in connection with the stress-strain curves and with hand tests, gave a comparison of rate of cure before and after aging. It was found that at 3 months 33 per cent of the samples had become faster curing than originally, at 6 months this percentage had increased to 45 per cent, and at 9 months to 50 per cent, with a corresponding decrease in samples showing a slower rate of cure.

The stress-strain curve showed a decided tendency to become steeper with increased aging time, which is an added indication of the faster rate of cure noted above.

Table II—Change in Shape of Stress-Strain Curves after Aging

	3 MONTHS	6 MONTHS	9 MONTHS
	%	%	%
Flatter	14	2	6.5
Steeper	37	56	87.5
No change	49	42	26

Action of Aged Rubber in Factory Stocks

When compounded in regular factory stocks, the aged rubber was found to act practically the same as stocks containing freshly milled rubber, on mills and calenders. However, in comparing regular factory runs of tube stock, it was found that the former was much rougher, more porous, and slower tubing than the latter. The physical tests showed the Williams plasticity figure to be equal to or lower than in the freshly milled stock, indicating a smoother, faster tubing compound. The modulus figure was higher in the stock containing the aged rubber, it was also slower curing even though the rubber itself seemed to be faster curing. This is explained by the fact that the rubber used in the tube stock had been aged only 3 months or less and the trend toward faster rate of cure was not yet so noticeable.

Since rough tubing could not be explained by a slower curing

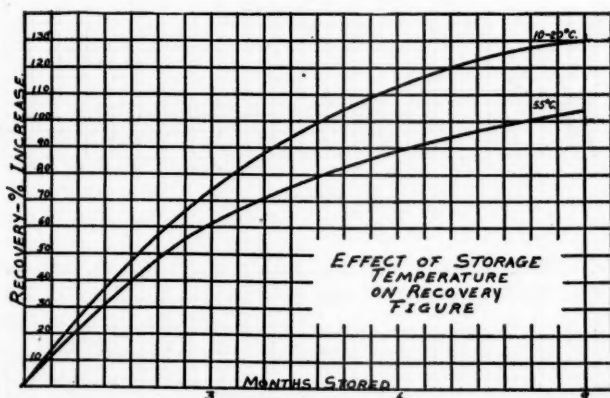


Figure 2

stock and since higher modulus is not necessarily a cause of rough tubing, the question of the low Williams plasticity figure is interesting. It appears that the Williams machine, being a compression type plastometer, is entirely satisfactory as a gage of milling and calendering operations, but in dealing with a tubing machine it is necessary to use a different type, such as the extrusion plastometer, which approximates more nearly actual tubing principles. When samples of tube stock containing aged rubber were compared with samples containing freshly milled rubber on an extrusion type plastometer, they were found to have a higher plasticity figure in the same degree as their action on the tubing machine would lead one to expect.

Age Tests on Aged Rubber

Samples of rubber from a number of bales were put up in the testing formula previously used.

Modulus tests were run on the fresh stock and on the same stock after 12-day oxygen and nitrogen aging. After 9 months' aging at -5.6° and at 55° C. the bales were re-sampled and retested both before and after 12 days' oxygen and nitrogen aging. The results were as follows:

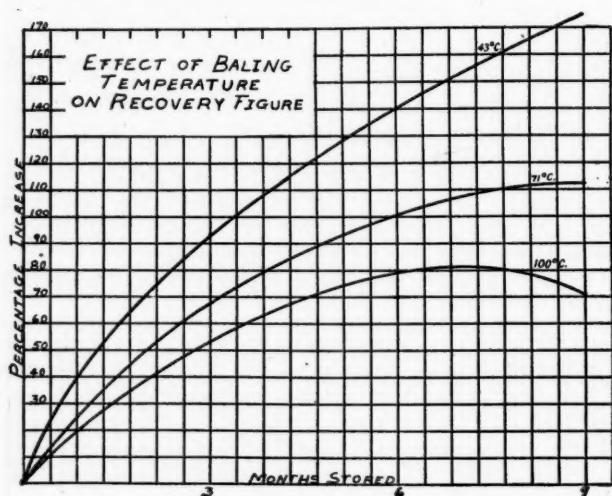


Figure 3

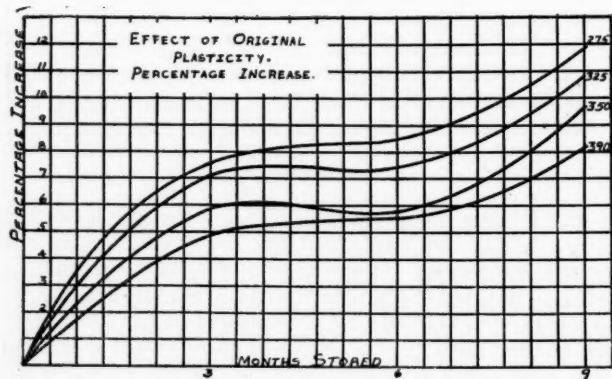


Figure 4

(1) The aged rubber conformed to the general average of all stored rubber; i. e., modulus and tensile were higher after storage than before. The rate of cure was somewhat faster.

(2) Aged rubber after 12-day nitrogen bomb test in the testing formula was much poorer aging than the fresh rubber. In most cases the modulus and tensile were much higher and the cure faster in the stored rubber than in the fresh rubber. In three samples the stored rubber was completely ruined by the age test, whereas the same rubber when fresh had withstood this test.

(3) The 12-day oxygen test was not so severe on the stored

rubber as the nitrogen bomb had been. Nevertheless, the samples were all inferior to the same rubber when fresh.

(4) The logical conclusion to be drawn from this is that the natural antioxidant has been destroyed by storage.

Change in Chemical Properties of Aged Rubber

A change in chemical properties of rubber is sometimes an indication of the nature of physical changes taking place. Table III shows the chemical changes occurring in several bales.

Table III—Chemical Changes in Rubber on Storage for 9 Months

BALE	ACETONE EXTRACT		ALCOHOLIC KOH EXTRACT		ACID NUMBER		N ₂ IN EXTRACT		N ₂ IN EXTRACTED RUBBER	
	Before	After	Before	After	Before	After	Before	After	Before	After
	%	%	%	%			%	%	%	%
Stored at -5.6° C.										
165	3.50	3.37	0.35	1.10	370	297	0.015	0.021	0.53	0.44
167	3.40	3.32	0.30	1.00	360	273	0.014	0.025	0.53	0.42
168	3.50	3.10	0.40	0.95	362	204	0.010	0.016	0.56	0.38
173	3.55	2.98	0.45	0.90	230	204	0.014	0.018	0.46	0.39
Stored at 55° C.										
174	3.65	3.20	0.35	1.07	266	236	0.011	0.015	0.52	0.40
175	3.60	3.25	0.42	0.85	275	205	0.011	0.015	0.52	0.33
176	3.75	3.45	0.48	1.25	233	217	0.010	0.014	0.59	0.43

The effect of storage is exactly the opposite of the effect of heat on rubber (4) except in nitrogen distribution. In the latter case the acetone extract and acid number increased. The decreased acid number and acetone extract may be due to a polymerization of part of the fatty acids, making them acetone-insoluble. Weight is given to this theory by the increased alcoholic potassium hydroxide extract. Alcoholic potassium hydroxide would reverse the polymerization process and extract the fatty acids from the rubber. The fact that the alcoholic potassium hydroxide extract increased more than the acetone extract decreased may be explained by supposing that some other non-rubber constituents have been rendered soluble by aging. The change in nitrogen distribution is in line with what we would expect.

"Frozen" Rubber

Among the many peculiar properties of rubber, that of freezing and thawing has been little investigated, in spite of its presence, during at least a part of the year, in this climate. It is occasionally encountered in midsummer and in rubber shipped direct from the plantations. Van Rossem and Dekker (5), as a result of a study of frozen smoked sheets, advanced the theory that the cause of the frozen conditions was crystal growth. The density, hardness, and light adsorption of frozen rubber at various low temperatures were suddenly decreased at about 36-38° C., indicating a melting of crystals. They evidently did not encounter frozen rubber of the type which has not been exposed to freezing temperature. Leblanc and Kröger (3) and Kröger (2) used sufficient pressure on rubber to cause a change of state (aggregation) which

they regarded as analogous to the effect produced by cold and, in a way, resembling vulcanization.

Apparently, milled rubber undergoes the same change as smoked sheets. Several bales of milled rubber were placed in a local ice plant at -5.6°C . and examined at various intervals during 38 weeks. The bales showed normal cooling curves and came to equilibrium in 4 to 6 days, depending upon their original temperature. When removed from the ice plant, the bales thawed in 5 to 7 days at room temperature varying from 15° to 30°C .

Frozen rubber, whether in sheet or milled form, assumes an opaque, creamy color and becomes very difficult to work. This condition may be either permanent or temporary. By the former is meant rubber which remains unworkable, boardy, and opaque at room temperature; and by the latter, rubber which will thaw at room temperature. Most frozen

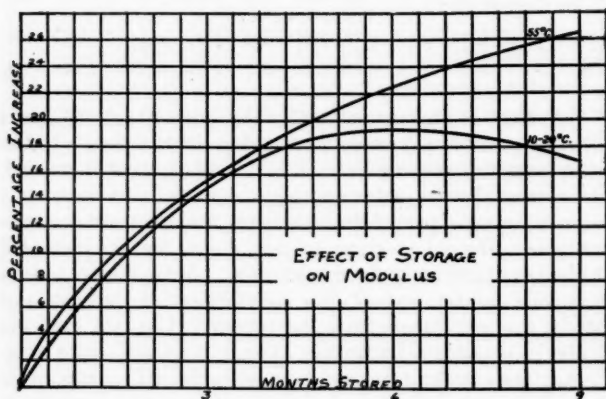


Figure 5

rubber is in the second class. Both usually have the same appearance, although bales of smoked sheets may assume their natural brown color and still remain boardy. By cutting a sheet the opaque, creamy color will be seen on the freshly cut edge.

The thawing of frozen rubber is a very definite temperature effect. A single sheet of permanently frozen crude rubber will remain boardy for months at room temperature. If placed in an oven at 50°C ., it will thaw in a few minutes. A piece of smoked sheet 3 inches square thaws in 2 minutes. Two adhering sheets, 3 by 3 inches thaw in 3 minutes; three sheets of the same size thaw in $4\frac{1}{2}$ minutes. This can be carried on up to the dimensions of a bale, which thaws completely in 24 hours if not surrounded by other bales.

The thawing of temporarily frozen rubber is a different type of change. Simple exposure to a moderate room temperature will thaw sheets in a few minutes. The thawing of a bale is,

of course, a longer process, but extreme temperature is not necessary except as a means of hastening heat transfer.

None of the baled, milled rubber was found to be permanently frozen, even after 38 weeks at -5.6°C . However, a number of 1-pound samples which were deformed by a rubber-cutting machine and later stored under slight pressure for nearly a year at room temperature ($5-35^{\circ}\text{C}$.) assumed the opaque, horny condition of permanently frozen smoked sheets and did not thaw out at room temperature. It would seem, therefore, that pressure is one cause of permanent freezing.

Acknowledgment

The writer wishes to express his thanks to G. K. Hinshaw and J. P. Maider for helpful criticism in the preparation of this article, and to R. P. Dinsmore for permission to publish it.

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Effect on Vulcanized Rubber Compounds of Immersion in Boiling Water¹

K. J. Soule

MANHATTAN RUBBER MFG. DIVISION, RAYBESTOS-MANHATTAN, INC.,
PASSAIC, N. J.

Vulcanized rubber finds many industrial applications in contact with or immersed in hot water. A study of its behavior in boiling water has shown that some rubber compounds continue to absorb water and swell after 10,000 hours' immersion in boiling water, without showing any signs of disintegration. Various fillers have different effects on the water absorption. Of the 35 fillers tested, 12 decrease the water absorption and 23 increase it. Carbon black shows the lowest absorption and ultramarine blue the highest.

A determination has been made of the loss of cutting resistance brought about by prolonged immersion in boiling water. While there is not perfect agreement between amount of water absorption and percentage cutting resistance loss, in general the stocks having the lowest water absorption show the least loss in cutting resistance, and vice versa.

ALTHOUGH to the general public "rubber" is considered to be unaffected by water, most rubber technologists know that vulcanized rubber is not water-proof and is more or less adversely affected by immersion in water, the extent of the deterioration depending upon the composition of the rubber compound, the temperature of the water, and the period of immersion.

Most of the published data on the water absorption of rubber compounds deal with water at ordinary temperatures,

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the authors being mainly interested in the possibility of the use of rubber in submarine cables. In this category we may place the work of Boggs and Blake (1), Williams and Kemp (6), and Kemp (3). Since the experimental work covered by this paper was started Winkelmann and Croakman (7) have reported the influence of various fillers, reclaimed rubber, etc., on the water absorption of rubber compounds. Their determinations were also carried out at room temperature. In none of the literature, however, has there been found any detailed report of the effect on cured rubber of continued immersion in boiling water or water at relatively high temperatures. In view of the many classes of rubber goods, such as valves, hose, packing, hot water bags, etc., which function in contact with hot water, such a study seemed to be of more than academic interest.

Experimental Method

Slabs 0.1 inch (0.25 cm.) thick were press-cured, and from them were cut pieces 2 inches (5 cm.) square. These pieces were weighed on an analytical balance and immersed in boiling water under a reflux condenser. At the end of each specified period they were removed from the water, blotted dry on the surface with a towel, and weighed.

$$\text{Volume of each piece} = \frac{\text{original weight in grams}}{\text{specific gravity}}$$

$$\text{Weight after immersion} - \text{original weight} = \text{gain in weight} \\ \text{increase in volume}$$

$$\frac{\text{Increase in volume}}{\text{Original volume}} = \text{per cent swelling}$$

Obviously, the increase in volume is not strictly equal to the gain in weight, as the pieces of rubber lose weight slightly owing to some leaching out of filler, soluble constituents of the rubber, etc. However, such losses are small compared with the amount of water absorbed, and are well within the experimental error of the determination.

Preliminary Tests

The first stocks tested were four regular factory compounds: No. 13, cheap, heavily loaded, high in alkali reclaim; No. 2, good-quality, high zinc oxide; No. 1, pure gum; and No. 234, medium-quality, high thermatomic carbon. These stocks had nothing in common as regards acceleration, rubber percentage, or volume loading. The progress of the swelling, or volume increase, of these stocks is shown in Figure 1.

Although later results showed that the wide differences in water absorption were not unusual, at the time the spread appeared to be surprisingly wide. The swelling of No. 13 rapidly reached an equilibrium, after which the changes in volume were very small and were both positive and negative.

Three of the stocks, however, were still showing steady swelling after 10,000 hours' immersion in boiling water. At the end of this time these three stocks were soft and pliable, without showing any signs of disintegration.

Effect of Pigmentation

To determine the effect of the separate addition of various fillers on the water absorption of a given base compound, the following control mix was made:

	Parts
Smoked sheet.....	100
Diphenylguanidine.....	1
XX zinc oxide.....	9
Sulfur.....	3

A 113-pound (51.25-kg.) batch of this base stock was mixed on a 60-inch (152.4-cm.) mill, and to 113-ounce (3.2-kg.) portions were added "30 volume" loadings of each of the following fillers on an 18-inch (45.7-cm.) laboratory mill:

No.	NAME	No.	NAME
1	American process XX zinc oxide	21	Carbon black (Micronex)
2	French process zinc oxide	22	Carbon black (Cabot)
3	"Special" zinc oxide	23	Dixie clay
4	Bleached barytes	24	Chromium oxide
5	Natural barytes	25	Cornstarch
6	By-product whitening	26	Titanium oxide
7	Sussex whitening	27	"Lead iron" green (mixture of lead chromate and ferroferri-cyanide)
8	Chalk whitening	28	Tuscan lake
9	Ultramarine blue	29	Iron yellow (hydrated iron oxide)
10	Magnesium carbonate	30	Iron oxide (Spanish)
11	Kadox	31	Lithopone
12	Iron oxide (domestic)	32	Aluminum flake
14	Sublimed blue lead	33	Lime
15	Lampblack	34	Asbestine
16	Soapstone	35	Powdered graphite
17	Heavy calcined magnesite	36	Sublimed white lead
18	Thermatonic carbon		
19	P-33		
20	Zinc oxide (St. Joseph Lead Co.)		

Curing, preparing, and boiling were carried out as previously described, the cure chosen in each case being that which had previously been found to give the optimum tensile. Figure 2 shows the time-swelling curves for a few of the fillers as well as for the control stock. In all cases the swelling is rapid at first, but gradually decreases as the immersion is continued. In this respect the behavior parallels the swelling of cured rubber in solvents as reported by Scott (5), who terms the initial rapid swelling the "swelling maximum," and the relatively slow later swelling, the "increment."

The complete results of the swelling determinations are shown in Table I, the listing being in the order of increasing swelling. Of the 35 compounds tried, 22 show lower water absorption than the control, while 13 give figures which are definitely higher. We should, however, take into account the fact that the loaded stocks have only 74.6 per cent rubber by volume, while the control contains 95.0 per cent. In order to get a true comparison it is necessary to divide the percentage of swelling by the percentage of rubber by volume in each stock. The data shown in Table II and Figures 3

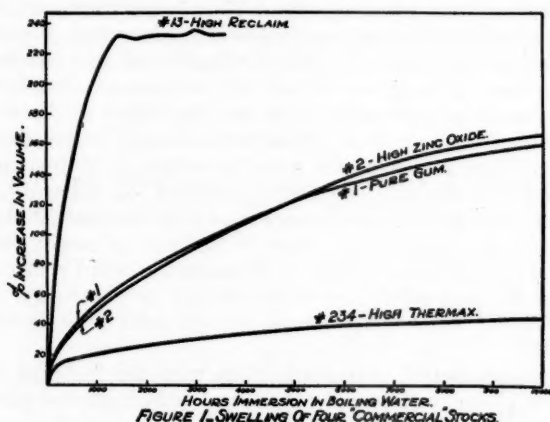


FIGURE 1-SWELLING OF FOUR COMMERCIAL STOCKS.

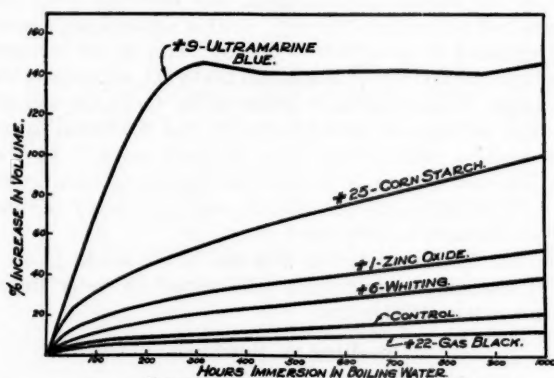
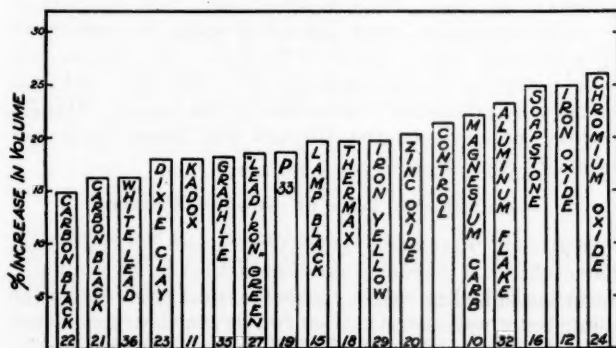


FIGURE 2-SWELLING OF CONTROL & 30 VOLUME STOCKS.

VULCANIZED RUBBER STOCKS-30 VOLUME LOADINGS.
FIGURE 3-EFFECT OF 1000 HOURS' IMMERSION IN BOILING WATER.

and 4 were obtained in this way. Thus, instead of there being 22 compounds showing lower water absorption than the control, there are only 12. This finding is not in agreement with that of Boggs and Blake (1), who were not able by compounding appreciably to lower the water absorptivity of rubber, or with that of Winkelmann and Croakman (7). Of the fillers studied by the latter investigators, thermatomic carbon was the only one which decreased the absorption of water, whereas the present work shows that at least 12 fillers accomplish this purpose. Some of these—e. g., carbon black and clay—were also studied by Winkelmann and Croakman. Some of these differences in results may be due to the use of different water temperatures, but the point merits further study.

For purposes of comparison, there were also included two 2-inch (5-cm.) squares of commercial ribbed smoked sheet, measuring 0.131 inch (0.331 cm.) in thickness. Both samples showed volume increase in 1000 hours approximately double that of the vulcanized pure gum, and although they both became soft and rather "tender," neither showed any signs of disintegrating or going into solution. This is not in agreement with the findings of Boggs and Blake (1), who report that pale crepe, "when soaked in water at 70° C. at the end of a few days becomes too sticky to weigh, and if allowed to continue soaking, disintegrates into a gluey mass." In their case, however, the crude rubber had previously been heated in a mold for 30 minutes at 100° C., which probably accounts for the difference in behavior.

Another interesting fact is that two of the stocks (Nos. 14 and 9) reached an equilibrium with respect to water absorption in less than 1000 hours.

Swelling vs. Hardness

From their work with rubber stocks of various hardnesses, Schumaker and Ferguson (4) have concluded that the rate of diffusion of water through rubber decreases greatly with an increase in hardness. Since water diffusion must be preceded by water absorption, water absorption would be expected to follow the same rule. This is not the case. For example, the stocks occupying the 1st, 2nd, 5th, 8th, 11th, 12th, and 28th positions had practically identical durometer readings, 69 to 72, whereas the stocks in the 4th and 36th places both had durometer readings of 60.

Compression Tests on Swollen Rubber

An attempt was made to study the changes in the physical characteristics of the rubber stocks brought about by continued immersion in boiling water. Since the effect produced by the boiling water was due to at least two factors, heat and water, it was thought worth while, if possible, to separate the two influences. Therefore, tests were made on rubber stocks which had been exposed separately in boiling water for 100 hours

and in a bomb at 100° C. in an atmosphere of carbon dioxide at 100 pounds (43.3 kgs.) pressure. Thus one set of samples would be affected by both water and heat and the other only by heat. The results are not very conclusive, although in most cases the water seems to produce a much greater effect than the heat alone.

Table I—Volume Increase Caused by Immersion in Boiling Water

Stock	TIME OF IMMERSION					
	48 hours	200 hours	400 hours	600 hours	800 hours	1000 hours
	%	%	%	%	%	%
22	3.3	5.9	7.9	9.2	10.3	11.0
21	3.8	6.5	8.6	10.0	11.2	12.1
36	2.7	5.7	8.2	10.0	..	12.2
23	3.0	6.2	8.3	10.2	11.8	13.4
11	3.3	6.2	8.6	10.7	12.2	13.4
35	3.1	6.3	8.6	10.3	..	13.5
27	3.9	7.6	10.3	12.0	13.2	13.9
19	3.2	6.3	8.5	10.9	12.5	14.0
15	3.4	6.6	9.1	11.5	13.1	14.7
18	3.2	6.4	8.9	11.5	13.1	14.7
29	3.7	7.3	10.2	12.0	13.7	14.8
20	3.5	6.7	9.3	11.9	13.7	15.3
10	3.0	6.9	9.8	12.1	14.5	16.6
32	4.1	8.4	11.4	13.8	..	17.5
16	3.4	7.4	10.6	13.9	16.4	18.7
12	3.9	7.9	11.5	14.6	16.7	18.7
24	4.3	8.6	12.4	15.2	17.5	19.5
7	3.5	7.8	11.4	14.1	17.0	19.6
31	4.2	8.3	11.7	14.2	..	19.8
34	3.9	8.4	11.8	14.5	..	20.1
30	4.6	9.4	14.0	15.4	16.8	20.2
2	5.3	10.1	13.4	16.0	17.9	20.3
Control	4.3	8.6	12.2	15.1	18.0	20.5
28	4.3	9.2	14.0	17.5	20.1	23.0
8	4.1	9.7	14.1	17.5	20.5	24.5
5	4.7	10.4	14.8	17.8	21.1	25.5
3	6.1	13.2	17.3	20.0	22.4	25.8
26	5.9	11.7	17.2	21.6	25.0	28.6
4	5.8	12.4	17.4	20.7	24.3	29.2
17	11.2	18.7	24.6	29.5	33.2	36.0
6	7.5	16.5	23.8	28.9	33.8	38.4
Crude rubber	6.8	30.4	..	45.0
1	12.3	25.5	34.8	40.7	46.9	55.5
25	22.6	43.5	62.6	75.6	86.4	100.0
33	14.0	39.0	59.8	80.0	..	110.0
14	24.6	54.2	81.3	101.5	111.5	116.0
9	30.4	122.4	144.0	141.0	140.0	145.0

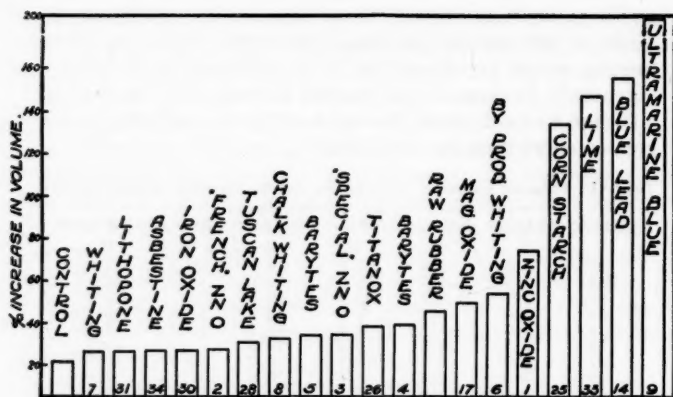
A compression machine developed by Henry L. Scott Company and the Bell Telephone Laboratories (2) was chosen for these tests. It has the merit of being autographic and drawing surprisingly reproducible curves. A wedge designed by L. A. Edland, of the R. T. Vanderbilt Company, was used as the compressing member. It was of soft steel, having a 90-degree angle with a cutting face 2 inches (5 cm.) long and 0.008 in. (0.02 cm.) wide.

It is not practical to show the compression curves for all of the stocks, but curves for a few of the most unusual are given, as follows:

Figures 5 and 6. Control and stock No. 19 (P-33), respectively. The curves are very similar, the modulus of No. 19 being consistently higher.

Figure 7. Stock No. 29 (iron yellow). The modulus of the three curves is identical and the cutting resistance practically unchanged by the water immersion.

Figure 8. Stock No. 23 (Dixie clay). Cutting resistance and modulus of both bombed and boiled stocks higher than the original.



VULCANIZED RUBBER STOCKS - 30 VOLUME LOADINGS.
FIGURE 4 - EFFECT OF 1000 Hrs. IMMERSION IN BOILING WATER.

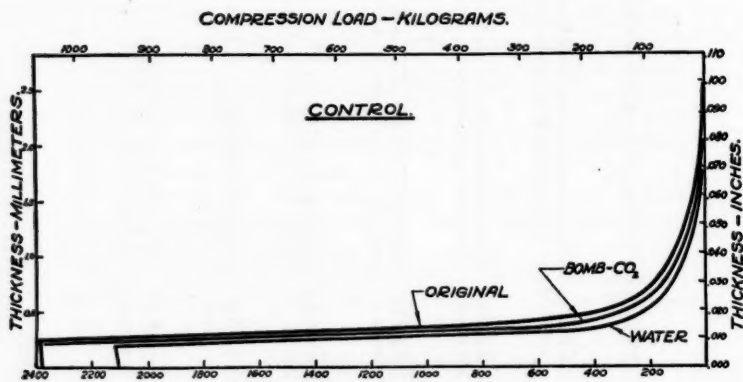


FIGURE 5 - EFFECT OF WET & DRY HEAT - 100 Hrs.

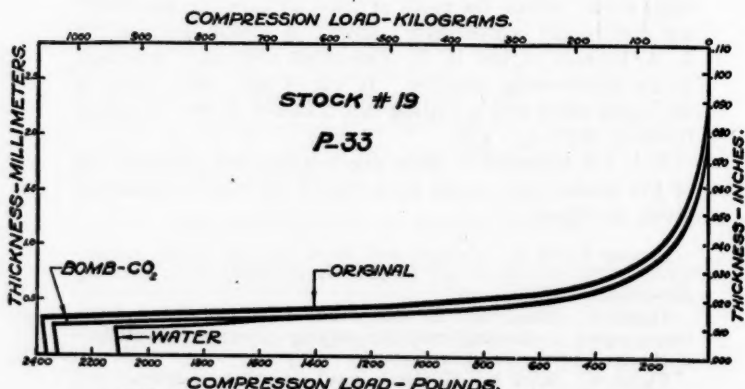
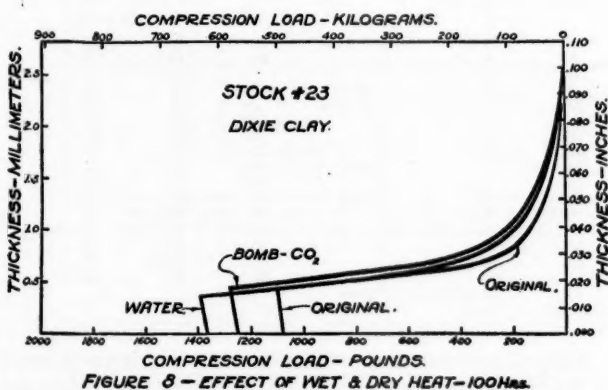
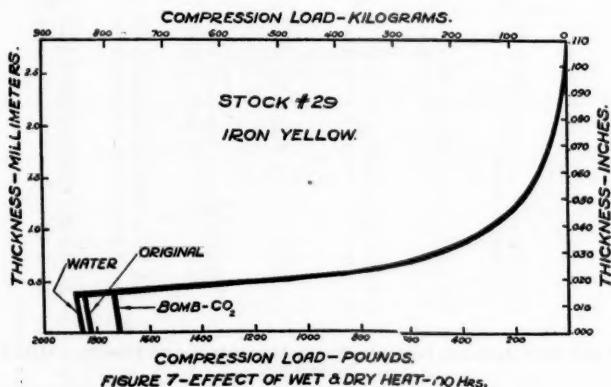


FIGURE 6 - EFFECT OF WET & DRY HEAT - 100 Hrs.

Figure 9. Stock No. 9 (ultramarine blue). An example of greatly diminished cutting resistance due to the effect of boiling water. Note the irregular curve for the water stock; this is typical for an excessively softened and swollen sample.

The principal point of interest was to see whether or not the stocks showing lowest water absorption also showed the least loss in cutting resistance after water immersion, and vice versa. The results are shown in Table III and Figures 10 and 11.



It will be noticed that fillers 22 and 21, the leaders with regard to water absorption, by no means lead with respect to loss of cutting resistance after water immersion—in fact, they place 23rd and 28th, respectively. This marked change may be due to heat aging rather than to the effect of the water. This is borne out by the high loss of cutting resistance in the carbon dioxide bomb; also to the behavior of stocks 27 and 28, which were only moderately affected by the water immersion and yet failed entirely in the carbon dioxide bomb. Both of these materials are known to age very poorly. How-

ever, all the other nine stocks which showed less water absorption than the control also show less cutting resistance loss. The same five stocks also show the poorest results in both classifications.

Table II—Swelling Caused by Immersion in Boiling Water
(Results based on volume of rubber present in each stock)

Stock	TIME OF IMMERSION			Stock	TIME OF IMMERSION		
	48 hours	600 hours	1000 hours		48 hours	600 hours	1000 hours
	%	%	%		%	%	%
22	4.4	12.3	14.8	31	5.6	19.0	26.5
21	5.1	13.4	16.2	34	5.2	19.5	26.9
36	3.6	13.4	16.3	30	6.2	20.6	27.1
23	4.0	13.7	18.0	2	7.1	21.4	27.2
11	4.4	14.4	18.0	28	5.8	23.4	30.8
35	4.2	13.8	18.2	8	5.5	23.4	32.8
27	5.2	16.1	18.6	5	6.3	23.8	34.2
19	4.3	14.6	18.8	3	8.2	26.8	34.6
15	4.6	15.4	19.7	26	7.9	29.0	38.3
18	4.3	15.4	19.7	4	7.8	27.8	39.1
29	5.0	16.1	19.8	Crude rubber	6.8	30.4	45.0
20	4.7	16.0	20.5	17	15.0	39.5	48.3
Control	4.5	15.9	21.6	6	10.1	37.4	52.7
10	4.0	16.2	22.3	1	16.5	55.0	74.0
32	5.5	18.5	23.4	25	30.3	101.0	134.0
16	4.5	18.6	25.0	33	18.8	107.0	147.0
12	5.2	19.6	25.0	14	33.0	136.0	155.5
24	5.8	23.4	26.1	9	41.7	189.0	193.0
7	4.7	18.9	26.3				

Table III—Relation between Water Absorption and Loss in Cutting Resistance

Stock	LOSS IN CUTTING RESISTANCE		Stock	LOSS IN CUTTING RESISTANCE	
	100 hours boiling H ₂ O	100 hours 100° C. CO ₂		100 hours boiling H ₂ O	100 hours 100° C. CO ₂
	%	%		%	%
23	26 gain	15.5 gain	34	13	20
29	1	6	16	15	0
32	0	12	2	15	0
8	0	6 gain	5	16	11
26	1	4.5 gain	3	19	0
12	2	3	22	19	27
18	3	2	4	20	11
36	3.5	19	17	21	29
31	4	2 gain	6	24	12.5
15	4.5	2	24	25	13
20	6	7 gain	21	26	26
10	6.5	12	1	30	5
7	8	13	9	35	8 gain
30	9.5	5	25	42	9
19	10	2	14	46.5	5
35	10	11	33	59	16.5
11	10 plus	0 plus			
Control	12.5	0			

Water absorption and swelling are effective in the interior of the rubber samples as well as on the surface, while the cutting resistance is influenced to a great extent by the character of the surface, particularly when that surface is softened by water immersion. It is not surprising, therefore, that there is not better agreement between the amounts of water absorption and the losses of cutting resistance. Indeed, the degree of agreement is remarkably good.

Summary of Results

Certain vulcanized rubber stocks are shown to still continue to absorb water after 10,000 hours' immersion in boiling water. There is a similarity between the swelling of cured rubber

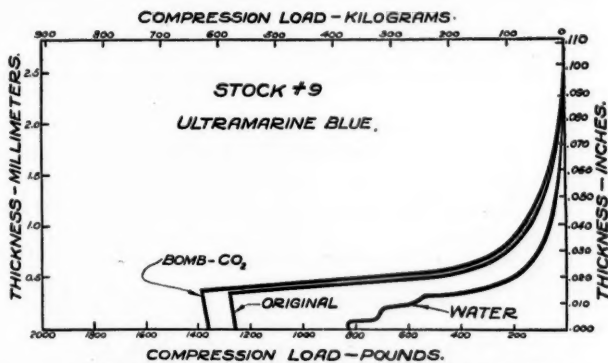
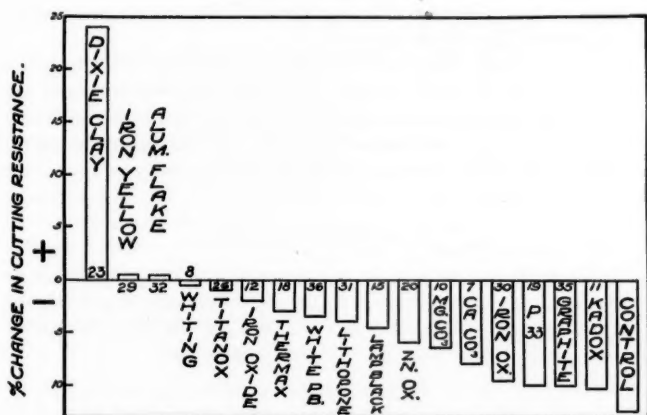
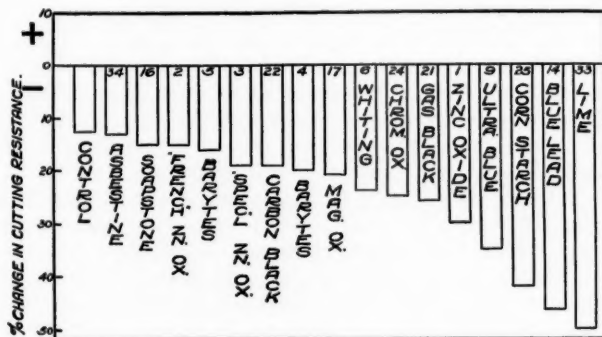


FIGURE 9-EFFECT OF WET & DRY HEAT-100 HRS.



VULCANIZED RUBBER STOCKS-30 VOLUME LOADINGS.
FIGURE 10-EFFECT OF 100 Hrs. IMMERSION IN BOILING WATER



VULCANIZED RUBBER STOCKS-30 VOLUME LOADINGS.
FIGURE 11-EFFECT OF 100 Hrs. IN BOILING WATER.

in boiling water and in rubber solvents. In both cases there is a rapid initial swelling followed by a gradually decreasing rate of swelling.

Of the 35 fillers studied, 12 are shown to decrease the water absorptivity of rubber.

Crude rubber in boiling water absorbs water to a much greater extent than cured rubber, but up to 1000 hours shows no signs of disintegrating.

Swelling in boiling water does not vary directly or inversely as the hardness.

In general, loss in cutting resistance varies directly with the amount of water absorption.

Conclusion

Further work is very desirable on the effect of different accelerators, antioxidants, and fluxes. It is possible that their study will throw more light on the mechanism of the swelling phenomena, and also help to explain the anomalous behavior of some of the fillers tested.

It would also seem to be worth while to study the action of a few selected stocks in water, at several temperatures between room temperature and 100° C., to determine if the water absorption and swelling merely increase with rising temperatures, or whether there might be an actual change in behavior at different temperatures.

Acknowledgment

Thanks are due the R. T. Vanderbilt Company for their kindness in permitting the use of their machine for the compression tests, and to L. A. Edland, of the same company, for valuable assistance in making these tests.

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- (2) Ingmanson and Gray, *India Rubber World*, **83**, 53 (1930).
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Rate of Deposition of Latex on Porous Molds¹

H. W. Greenup

FIRESTONE TIRE & RUBBER COMPANY, AKRON, OHIO

The effects of pressure, rubber concentration of latex, temperature, and hydrogen-ion concentration upon the rate of deposition of latex on porous molds are described. Pressure, rubber concentration, and temperature were found to be negligible factors in comparison with hydrogen-ion concentration. By adjusting the pH of the latex to 6.1 it was found possible to obtain aggregation of the latex particles and a marked increase in rate of deposition.

THE manufacture of rubber articles by dipping porous forms in latex was first described by Condamine (5). He reported to the Paris Academy in 1736 that the natives in South America made such articles as shoes and bottles, using clay molds which, after drying of the deposited layer, were shattered and removed. The idea of making articles by a process of this sort, instead of by coagulating the latex, milling, and then shaping the milled rubber, appeals to the imagination. Increased tensile strength and improved aging have been claimed (10) for articles made directly from latex, and their remarkable resistance to tear, obtained under certain conditions, is well known.

In more recent years there has been a revival of interest in this method of manufacture, to judge by the number of patents issued. Ditmar (2) and also Hopkinson (12) have patented a process for making articles such as surgeons' gloves, inner tubes, etc., by deposition on porous forms. Venosta (20) used concentrated latex to lessen the number of

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dips necessary with a non-porous mold. The Dunlop Company (3) has attempted to hasten deposition by using a porous mold filled with a coagulant-containing gel, while the Anode Rubber Company (1) has impregnated the mold with a coagulant which diffuses outward through the still permeable, coagulated layer. Hauser (9) has used filtration through porous ceramic filters as a method of concentrating latex, but he states (8) that there are too many drawbacks to permit its being used commercially on the plantations. However, Stevens (18) is of the opinion that systematic experiments with differently prepared collodion filters might yield a method of quickly and cheaply filtering, and thereby concentrating, latex.

Latex usually contains particles varying in size from 0.5 to 3μ , with some of ultramicroscopic size. As the average pore size of an ordinary grade of filter paper is 3.3μ (16), latex passes through unchanged until a sufficient number of particles have been adsorbed on the pore walls to cause stoppage. This is not the case with unglazed porcelain filters of the Chamberlain type, where the size of the largest pores is from 0.2 to 0.4μ (16). It would seem that filtration would be fairly rapid at first, but would become slower with increasing resistance to flow of serum through the deposited layer. Undoubtedly, some of the ultramicroscopic particles would be drawn into the pores and, being adsorbed on the walls, contribute to the decrease in the rate of filtration. Another factor to be considered, especially when working with pressure, is the deformability of the latex particles.

In view of the fact that the literature offers no detailed information as to the effects of pressure temperature, rubber concentration, or hydrogen-ion concentration, the effect of these factors on latex deposition on porous molds was investigated.

Experimental Procedure

The apparatus illustrated in Figure 1 was used. It consisted of a 24-inch (68.5-cm.) piece of galvanized 4-inch (10.15-cm.) pipe, *A*, closed at each end with caps, *B*. A 0.25-inch (6.35-mm.) pipe, *C*, led from a vacuum line through the bottom cap to the porous mold, *D*, to which it was joined by means of a rubber stopper, *E*. A 0.25-inch (6.35-mm.) side pipe, *F*, permitted the entrance of air either at atmospheric or higher pressure. When working above room temperature the water jacket, *G*, was added.

The porous molds were alundum extraction thimbles of medium porosity. They were 45 mm. in diameter and 127 mm. in length. Thimbles of coarse porosity allowed some latex to pass through, but those of medium porosity did not. They were relatively uniform, would stand an external pressure of at least 35 pounds per square inch (2.46 kg. per sq. cm.), and could be easily cleaned by ignition in a muffle furnace.

In performing the experiments the mold was first wet with

water to prevent the formation of an impermeable, dehydrated layer, the latex added, and the top cap screwed on. After deposition the top cap was unscrewed, the latex poured out, and the bottom cap and connected mold removed. The deposited layer was dried at 60° C. and its thickness determined.

Suction was applied to give pressure differences up to 7.5 pounds per square inch (0.52 kg. per sq. cm.) and above that air pressure was also used. All pressure differences were recorded as "pressure" whether due to a partial vacuum in the mold or a partial vacuum and air pressure on the latex.

Ammonia-preserved latex, containing 1 per cent ammonia and 35 per cent rubber (by coagulation), was used unless otherwise stated.

Time Required for Deposition

A preliminary experiment to determine the time necessary to obtain a deposit of appreciable thickness was first made. The results are shown in Table I.

Table I—Effect of Time on Thickness of Deposit	
Pressure, 7 lbs. per sq. in. (0.52 kg. per sq. cm.)	
TIME	THICKNESS OF DEPOSIT
Minutes	Mm.
30	0.3
45	0.55
840	1.38
1020	1.5

These preliminary tests demonstrated that deposition of this sort is too time-consuming to be considered commercially feasible. As expected, the rate of deposition was more rapid at the start than later, a deposit of 0.55 mm. being formed in the first 45 minutes, while the increase in thickness was only 0.12 mm. between 840 and 1020 minutes.

Effect of Pressure

The effect of pressure was first determined in attempting to hasten deposition. The pressure was first kept at 5 pounds per square inch (0.35 kg. per sq. cm.) for 3 minutes and then increased the desired amount. This prevented latex particles from being forced into the pores of the mold at the start, a condition which would have decreased deposition considerably. The results are shown in Table II.

Table II—Effect of Pressure on Deposition		
Time, 30 minutes		
PRESSURE	THICKNESS OF DEPOSIT	
Lbs./sq. in.	Kg./sq. cm.	Mm.
7.5	0.52	0.3
12.5	0.88	0.2
17.5	1.23	0.5
35	2.46	0.5

A pressure of 17.5 pounds per square inch (1.23 kg. per sq. cm.) caused an increase in thickness of the deposited layer of about 60 per cent over that obtained with a pressure

of 7.5 pounds per square inch (0.52 kg. per sq. cm.), but a further increase to 35 pounds per square inch (2.46 kg. per sq. cm.) did not cause a corresponding increase in thickness. One trial was started at a pressure of 50 pounds per square inch (3.5 kg. per sq. cm.), but was interrupted by the breaking of the mold. Pressures up to 35 pounds per square inch (2.46 kg. per sq. cm.) did not increase the rate of deposition sufficiently to bring it into the range of practical applicability.

Table III—Effect of Rubber Content of Latex on Deposition

Pressure, 35 lbs. per sq. in. (2.46 kg. per sq. cm.); time, 30 minutes

RUBBER CONTENT	THICKNESS OF DEPOSIT
%	Mm.
10	0.25
15	0.25
25	0.25
35	0.3

Effect of Rubber Concentration of Latex

In determining the effect of rubber concentration, the latex was prepared by dilution with distilled water; thus there was no change in the ratio of rubber to non-rubber constituents. The results are shown in Table III.

There was no change in speed of deposition upon dilution of the latex. Some experiments were made with latex mixtures of higher rubber content, with the result that thicker deposits were formed. The latex was concentrated by the Hauser evaporation process to a rubber content of 68 per cent. It contained 0.75 per cent potassium hydroxide and 0.75 per cent potassium-coconut oil soap. This was attributed to the increased viscosity of the mixtures and corresponding tendency for increased thickness of what might be termed "the undeposited but adhering" layer.

Effect of Temperature

As increased temperature ordinarily has a considerable effect upon the rate of filtration of liquids owing to decreased viscosity of the liquid, it seemed logical to assume that this would be the case in the filtration of latex. A water jacket was added to the apparatus (Figure 1) and experiments were made at different temperatures. The water jacket was heated with a gas burner and, after the latex had reached the desired temperature (20), pressure was applied. The results are shown in Table IV.

Table IV—Effect of Temperature on Deposition

Pressure, 27.5 lbs. per sq. in. (1.93 kg. per sq. cm.); time, 30 minutes

TEMPERATURE	THICKNESS OF DEPOSIT
° C.	Mm.
26	0.3
38	0.4
49	0.5
60	0.5
71	0.5

It was evident that decreased viscosity of the serum resulting from higher temperatures did not increase the rate

of deposition sufficient to merit further consideration. Experiments at temperatures higher than 71°C . were made, but difficulty was encountered due to the formation of a dried film at the surface of the latex. There was also some tendency for bubbles to form in the deposited layer after removal from the apparatus. Agitation would have lessened the tendency for the formation of a dried film on the latex, but not the formation of bubbles in the deposit.

Effect of Hydrogen-Ion Concentration

The effect of hydrogen-ion concentration on the rate of deposition was next investigated. As the hydrogen elec-

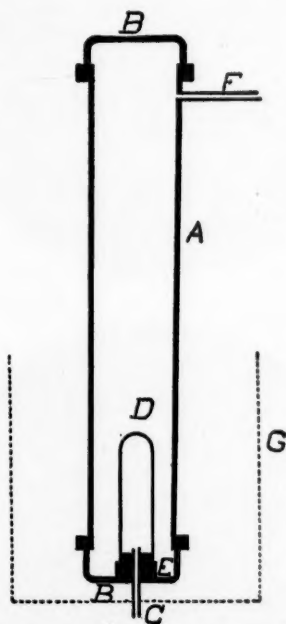
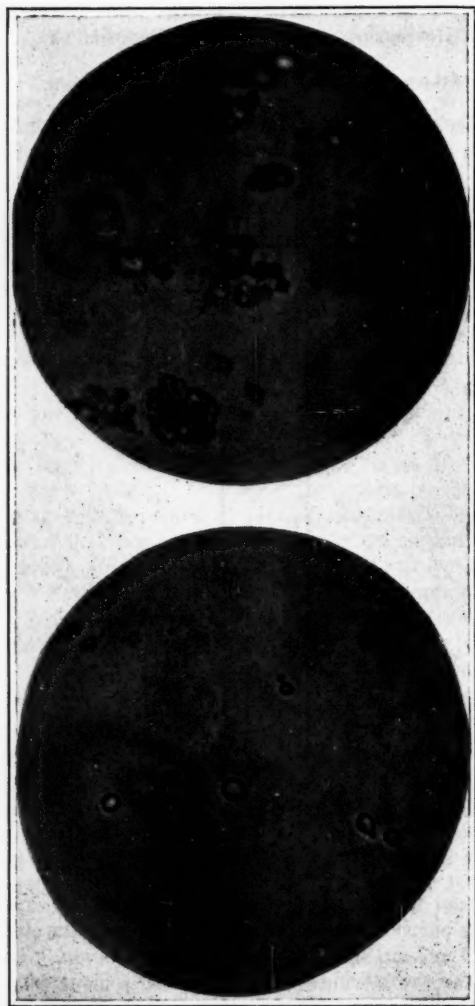


Figure 1—Deposition Apparatus

trode cannot be used to determine the pH of latex mixtures (6), owing partly to the deposition of rubber on the electrode, the Wulff colorimetric foil method was chosen. The foil method has the advantage of being less tedious and time-consuming than the spot-plate indicator method. An accuracy of 0.2 pH has been claimed for this method (10), but MacKay (15) has shown that there are certain ranges in which this is not true. One objectionable feature of the Wulff foil is the tendency for the indicator to diffuse into the latex especially if left in longer than 1 minute. McGavack and Rumbold (14) have recently used the glass electrode with considerable success, and it seems probable that this method

may overcome some of the difficulties in measuring the pH of latices.

Since latex starts coagulating at about pH 4.8 (7), it was necessary, in order to avoid local coagulation, to use an acid or buffer mixture which gave a pH value higher than 4.8



Untreated
Aggregated
Figure 2—Photomicrographs of Latex. 1500 \times

in the concentration used. Stevens (19) has stated that it is possible to avoid local coagulation in ammonia-preserved latex when using acetic acid if dilute acid is added with vigorous stirring, but this was not the experience of the writers working with 0.5 per cent solution. Boric acid, which has a pH of approximately 5 in 1 per cent solution at 25° C., was

chosen. It was later found possible to add a 10 per cent solution at 60° C. without causing local coagulation in the latex. Table V shows the results of deposition experiments.

Table V—Effect of Hydrogen-Ion Concentration of Deposition

Pressure, 35 lbs. per sq. in. (2.46 kg. per sq. cm.)

pH	TIME <i>Minutes</i>	THICKNESS OF DEPOSIT <i>Mm.</i>
11.2	30	0.25
10	30	0.25
8.1	30	0.38
6.1	10	1.27

The thickness of the deposited layer was increased about five times and the time decreased to one-third by changing the pH of the latex from 11.2 to 6.1. At the latter value there was a considerable increase in viscosity but no local coagulation. It was evident that a marked change had occurred in the properties of the latex.

The coagulation of latex has been said (10) to occur in the following steps: (1) The individual particles come together reversibly in small bunches (aggregation); (2) the small bunches come together irreversibly to form visible clumps (flocculation); (3) these clumps come together to form still larger ones (coalescence); and (4) the larger clumps come together to form the coagulum. Microscopic examination indicated that the addition of sufficient boric acid to give a pH of 6.1 had caused aggregation. Flocculation did not take place since it was possible to redisperse the particles by the addition of sufficient ammonia. This condition of aggregation is illustrated in Figure 2. Since the small bunches were several times larger than the original particles, they were more easily filtered out of the serum.

Note—Since this work was completed several patents have come to the attention of the writer. Aggregation of latex, or increase in filterability, may be caused by the addition of such materials as sodium phosphate buffer mixtures, calcium and other polysulfides, clays, Irish moss, etc., according to Hopkinson and Gibbons (13), Smith (17), and Hazell (11). The Dunlop Company (4) has also patented the manufacture of articles made of organic materials from aqueous dispersions in which the organic materials have been agglomerated by various materials.

It was possible to wash the deposited layer by replacing the aggregated latex with water and continuing the filtration. When the mold was removed from the deposition bath but left connected to the vacuum line, there was shortly afterwards a marked decrease in thickness of the deposited layer. This was due to syneresis or squeezing out of the enclosed serum. The deposited layer then became compact and non-porous.

Relatively large amounts of boric acid were required to produce this aggregation, as much as 10 per cent being added to a latex containing 1 per cent of ammonia, but by lowering the ammonia content through aeration this amount could be reduced considerably. The stability of aggregated latex was good, closed samples being kept as long as 12 months without appreciable change in degree of aggregation or any tendency for putrefaction.

Owing to the size of the aggregated clumps, Brownian movement was much slower or in some cases not evident. This explained the comparatively rapid creaming or separation into thick cream and clear serum layers. This cream could be redispersed by stirring.

Owing to the increased protective matter present, it was not possible to cause aggregation in concentrated latex by adjusting the pH to 6.1 with boric acid. By using Irish moss or similar materials a less complete aggregation may be accomplished. The filterability of the treated Revertex was not so great as that of the aggregated latex.

It has been found that considerable difficulty may be encountered in obtaining the exact degree of aggregation and consequent filterability when repeating experiments, especially if latices are used which have been obtained from different sources or from trees tapped shortly after a rest period. The addition of pigments will in some cases cause marked increase in the degree of aggregation. In view of these factors, the development of a process which always yields a latex in a definite state of aggregation would seem to be a difficult problem.

Acknowledgment

The writer wishes to acknowledge his indebtedness to N. A. Shepard for his helpful suggestions and willing counsel during the course of this work.

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Further X-Ray Studies of Gutta-Percha and Balata¹

Charles W. Stillwell and George L. Clark

DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ILLINOIS, URBANA, ILL.

New x-ray diffraction data for gutta-percha and balata are given and considered in the light of von Susich's recent conclusion that these substances are identical and exist in two crystalline forms. The data also support the assumption that gutta-percha is a mixture of balata and another crystalline constituent, an assumption that is in some respects preferable to that of von Susich. Although the relation between gutta-percha and balata has been established and there may be no ultimate difference between them, it is pointed out that the majority of specimens examined of material classified commercially as balata produce a diffraction pattern different from that of gutta-percha, a fact of practical significance.

THERE has been considerable disagreement as to the significance of x-ray diffraction data for gutta-percha and balata as reported by different investigators. The main point at issue has been the fundamental difference between gutta-percha and balata. Clark (1) and Hauser (2) have obtained different diffraction patterns for the two when unstretched, while Hauser has found them to be the same when stretched. Von Susich (3) has recently done much to clarify the problem. He reaches the conclusion, as a result of x-ray diffraction data, that gutta-percha and balata are identical, and that the substance exists in two different crystalline modifications, the alpha form being stable below about 60° C. and changing to the beta form when heated above this temperature. Of course, this at once explains Hauser's results, since the specimens were doubtless heated above 60° C. when stretched and would then show the beta pattern.

Independent data have been obtained in this laboratory

¹ Received January 17, 1931. Presented before the Division of Rubber Chemistry at the 81st Meeting of the American Chemical Society, Indianapolis, Ind., March 30 to April 3, 1931.

which, in the main, confirm the findings of von Susich and also help to explain further some of the discrepancies which have existed and do exist in the x-ray data for these two substances.

Several specimens of gutta-percha and balata have been examined. Debye-Scherrer patterns, using molybdenum radiation, have been obtained for all of them, and pinhole patterns, using copper radiation, have been obtained for some of them. It was suspected that the disagreement among the several investigators might be due to the fact that the materials examined were from different sources. The data presented herewith are for the following samples: Peruvian block balata, Surinam balata (smoked sheet), desinated balata (source unknown), and Macassar gutta-percha. (Von Susich (3) showed that it is not necessary to use purified gutta hydrocarbon. The same diffraction patterns are obtained for the pure and impure material, indicating that the diffraction pattern is that of the gutta hydrocarbon.) The diffraction patterns for these, together with those obtained by von Susich for α - and β -gutta-percha, are recorded in Table I. Before von Susich's work appeared, it had been suspected that gutta-percha was a mixture of balata and another crystalline constituent. This conclusion is supported by two facts:

(1) The balata pattern is to be found almost complete in the gutta-percha pattern, the position of the lines corresponding to within the experimental error with one, and possibly two, exceptions. The spacing of balata, which is noticeably different on the gutta-percha pattern, is the line 4.73–4.75 Å. which occurs at 4.56–4.68 Å. on the gutta-percha pattern. The fact that this line varies on the gutta-percha pattern tends to minimize the lack of agreement of this value with line 4.73–4.75 Å. on the balata pattern. The agreement seems to be more than a coincidence and is therefore suggestive of the interpretation which has been made above, but since the lines are not in perfect agreement the evidence is not necessarily conclusive.

(2) Patterns of an intermediate nature were frequently obtained, both for natural gutta-percha and in isolating chicle gutta (4) in which the intensity of the balata lines varied, indicating a variation of the concentration of balata in the whole gum.

The results of von Susich (3) throw a somewhat different light on the data of the present writers. It is evident that their gutta-percha pattern agrees very well with von Susich's pattern for α -gutta-percha, while the pattern they have always associated with balata is the pattern of his β -gutta-percha. The data are in satisfactory quantitative agreement, with two exceptions. The largest spacing for α -gutta-percha is too large to be found on the Debye-Scherrer diagram and has been obtained from the pinhole diagram; and it is evident that in von Susich's pattern and that of the writers the diffraction ring from which the value was calculated is so diffuse that no great accuracy can be expected. The value 4.56 Å. for α -gutta-percha is not very close to the present writers' corresponding value.

Von Susich states that β -gutta-percha may be converted into α -gutta-percha, the low-temperature form, by dissolving it and reprecipitating below 60°C . The specimens of de-resinated balata and Peruvian block balata were dissolved in benzene and the benzene was allowed to evaporate spontaneously. Each residue produced the pattern recorded in columns 9 and 10 of Table I, the typical pattern for gutta-percha.

We may still explain all the data at hand by assuming that the gutta-percha is a mixture of balata and another crystalline constituent, provided it is assumed that at the so-called transition temperature the second crystalline phase is dispersed in the balata and held in the amorphous state so finely divided that it produces no diffraction pattern. It seems very probable that this is exactly what happens to chicle gutta when chicle is refined. This explanation is favored by the fact that the transformation is not easily reversible. Von Susich finds that the low-temperature condition cannot be set up again by simply cooling the gutta-percha, but it must be dissolved and reprecipitated below 60°C . If a second crystalline phase were dispersed as the temperature was raised, this would not easily coagulate again when the temperature was lowered; but if the gum were dissolved and allowed to recrystallize, one would expect the two crystalline phases to develop and give their characteristic patterns. Regardless of whether we are dealing with two forms of gutta-percha or with a mixture of balata and another substance, the important facts of the case have been admirably set forth by von Susich. The significant difference in the present writers' interpretation depends on the suggestive, if not conclusive, evidence that the pattern for balata is to be found in the gutta-percha pattern, indicating that the gutta-percha is a mixture of balata, as such, and another crystalline form. Von Susich did not consider the possibility of a mixture. Based on his own interpretation, it would mean that his so-called α -gutta-percha is really a mixture of β -gutta-percha and another constituent.

It has been definitely shown that gutta-percha and balata give identical diffraction patterns at room temperature in some cases; that when the patterns at room temperature differ, the gutta-percha may be heated above 60°C . and will then give the characteristic balata (or β -gutta-percha) pattern; or the balata may be dissolved and reprecipitated below 60°C . to give the characteristic gutta-percha pattern. The fact remains, however, that for two of the three samples examined which are known commercially as balata, as well as for balata samples previously examined by Clark and Hauser, the diffraction pattern differs from that of samples of gutta-percha. Of course, only a limited number of specimens have been examined and it would be well to consider a greater number of so-called balata specimens. If the diffraction patterns differ from that of gutta-percha in a majority of cases this difference would be of practical significance as a

Table 1—Comparison of X-Ray Diffraction Data for Gutta-Percha and Balata with Data of von Susch for α - and β -Gutta-Percha

SURIAM d (Å.)	I	PERUVIAN BLOCK		d (Å.)	I	DERESINATE		MACASSAR GUTTA-PERCHA		RESIDUE FROM BENZENE EXTRACTION		α -GUTTA-PERCHA		β -GUTTA-PERCHA	
		d (Å.)	I			d (Å.)	I	d (Å.)	I	d (Å.)	I	d (Å.)	I	d (Å.)	I
4.97	vs							10.35	w		vs	12.2	vw		vs
								4.97	s			4.96	vs		
4.63	m	4.75	s			4.68	m			4.97	vs			4.73	vs
4.07	m									4.63	m	4.56	s		
3.93	s	3.93	s			3.92	s			4.07	m				
3.83	s					3.83	m			3.94	s	3.94	s	3.89	s
2.94	m	2.94	w			2.95	m			3.32	s	3.32	s	3.29	vw
		2.78	w			2.78	m			2.94	m	2.98	w	2.95	m
2.72	m	2.38	w			2.30	w			2.72	m	2.74	w	2.77	w
								2.73	w						
								2.38	w						

means of classification. Obviously, the discovery that one form may be converted into the other at will does not lessen the difference between the two forms, although it does explain this difference. It simply means that the product which is generally known commercially as balata is a gum, originally identical with gutta-percha, which has at some time, either when first coagulated or later, been subjected to a temperature above 60° C. and had its crystal structure and other physical properties changed thereby.

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Recovery of Rubber and Cotton from Uncured Tire Ply Scrap¹

Extraction Process

Charles S. Powell

FIRSTSTONE TIRE & RUBBER COMPANY, AKRON, OHIO

A new method for reclaiming uncured tire ply scrap is described. This is an application of the familiar solvent-extraction process. It possesses several advantages over the other methods of separating the rubber and cotton fabric in the scrap, particularly from the standpoint of waste of materials, for both the cotton and the rubber are completely reclaimed without deterioration. If the process is to have wide application, however, means must be devised for utilizing the dilute rubber cement produced.

THE utilization of tire trims has always been a difficult problem. Composed of uncured rubber and long staple cotton, their value is considerable. Certain quantities, after being broken down on a mill, can be used in bead covers, flaps, shoe soles, and mats without detrimental effects. The Dunlop Rubber Company (2) has been granted a patent covering a composition of uncured ply scrap, ground scrap, etc., to be used in the manufacture of objects of fibrous rubber.

Previous Methods

There are several methods in use for reclaiming the uncured tire ply scrap. In one method the cotton is washed from the rubber on a four-roll washer. The sheet of rubber passes between the four rolls, each passage exposing a fresh surface to the action of streams of water. A great deal of the cotton is removed from the rubber in this way, and the action of the

¹ Received March 16, 1931. Presented before a meeting of the Akron Rubber Group, February 9, 1931.

water is assisted by a wire buffing wheel, which is very effective in tearing the cotton away from the rubber. The rubber, after being dried, is used over again as skim stock, while the cotton may be dried and sold. A patent has been granted to T. F. Furness on a modified form of this process (3).

The acid process for reclaiming cured tire scrap was developed by Mitchell, between 1882 and 1889 (5), and has been adapted for use with uncured trims. The scrap as it comes from the tire-building room is treated with 25 per cent sulfuric acid in large wooden vats. The temperature is raised to 110° C. in about 2 hours by passing steam into the mixture or by means of steam coils. The acid is then drained from the scrap, which is then washed in the vats several times with water, and finally removed to a washing mill, where the remainder of the acid is removed. During the process the

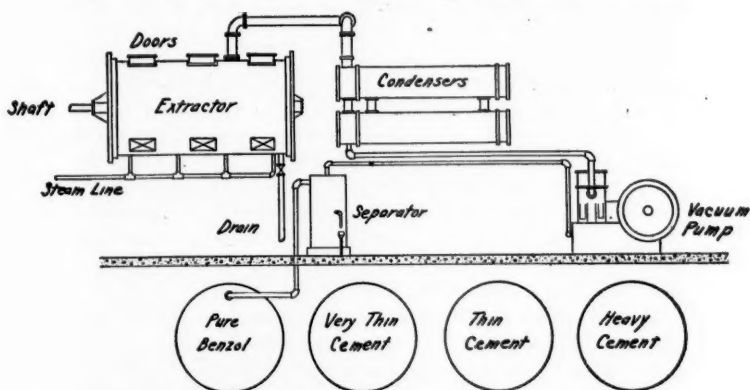


Figure 1—Diagram of Apparatus for Solvent Extraction of Uncured Tire Scrap

cotton is entirely disintegrated and the rubber is practically as good as the original skim stock, except that the accelerator and a large part of the zinc oxide have been destroyed. With the advent of the very active acidic accelerators in recent years, the acid process has been complicated by the necessity of a preliminary treatment with caustic to remove the accelerator, to prevent the stock from curing during the acid treatment. The acid process is therefore wasteful and expensive.

Development of Solvent-Extraction Process

There is nothing new about a solvent-extraction process. Extraction has been widely used in recovering oils and fats from various waste products. A somewhat related process was patented about ten years ago (1) for reclaiming cured tire scrap. The tires are immersed in solvent for 24 hours. At the end of this time the rubber is not dissolved, but swollen sufficiently to allow a separation of the fabric and rubber. Penfold (4) recommends treating uncured scrap by a solvent-

extraction method. The stock is pressed into blocks and then cut into slabs an inch thick. These slabs are then extracted twice with solvent and the cotton is centrifuged and dried.

An extraction process is quite simple as applied to uncured trims. The scrap and solvent are placed in a container and agitated. The rubber swells, goes into solution, and the cement produced is drained off. The cotton must then be rinsed with fresh solvent to remove the rest of the rubber. The difficulty in the process is in working out a safe, efficient method for removing the cotton from the cement. In the beginning an attempt was made to do this by putting the mixture of rubber cement and cotton into a hydraulic press and squeezing the cement through a screen. The screen soon became clogged, however, and the resulting pressure caused the cement to spurt from the top of the press. Moreover, it was rather difficult to transfer the mixture of cement and cotton from the mixer to the press. Furthermore, the pressed pulp had to be put back into the mixer and rinsed with fresh solvent. Experiments were also conducted using a centrifuge to remove the cement. This was satisfactory for a while, but the holes in the centrifuge became clogged with dried rubber and it was necessary to take it apart and burn out the rubber. This process was also inefficient, slow, and dangerous. It would have been almost impossible to carry out either of these processes on a large scale. Extraction equipment was then purchased,² and this is the plant, with numerous alterations, which is in operation today.

The extraction plant is shown in Figures 1 and 2. The extractor is 5 feet (1.52 meters) in diameter and 12 feet (3.65 meters) long and contains a revolving cage, lined with 30-mesh wire screen (wire diam. 0.013 inch). This cage revolves at about 11 r. p. m. and is provided with doors for charging and discharging.

To operate the extractor, it is rotated until the doors are opposite the doors at the top of the outer shell. The cage is then loaded with 1000 pounds of uncured tire ply scrap and both sets of doors are closed. The extractor is then filled with benzene through the charging line and the cage started rotating. At the end of about 2 hours the valve in the drain line is opened, with the cage still revolving, and the heavy cement is drained into the storage tank for heavy cement. The extractor is then filled again and washed for $\frac{1}{2}$ hour, and then drained as before. This second wash also goes to the heavy-cement tank. The next two washes are drained into the thin-cement tank and the last two washes go to the tank for very thin cement.

By this time the cotton, which contains less than 1 per cent of rubber, is quite white and clean. However, it contains about 300 gallons (1134 liters) of benzene, which does not drain off. For that reason it is necessary to steam the cotton after each run and recover the solvent. To assist in vaporiz-

² From Ernest Scott & Co., Fall River, Mass.

ing the benzene and to keep the temperature as low as possible, the system is provided with a vacuum pump. Steam at 50 pounds (3.51 kg. per sq. cm.) pressure is turned into the extractor through four nozzles at the bottom of the outer shell. The benzene is vaporized and passes over with the steam to the condensers, where they are both condensed and drawn to the vacuum pump which in turn delivers them to the water separator. In the separator the water, being heavier than the benzene, settles to the bottom, where it is drawn off, while the benzene runs off the top into the pure-benzene tank. In filling the extractor, instead of using pure benzene, thin cement is used for the first four washes. For the last two washes it has been found necessary to preheat the benzene to 140° F. (60° C.) before washing the scrap.

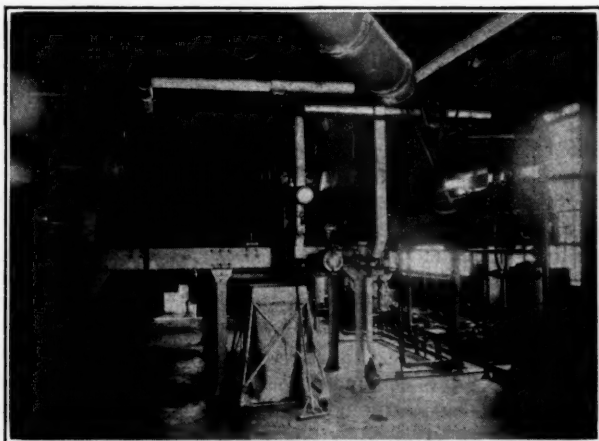


Figure 2—Solvent-Extraction Plant for Reclaiming Tire Scrap

The use of hot washes speeds up the process considerably and helps in obtaining a cotton with a low rubber content.

The cotton is removed through the lower doors of the extractor. It contains about 30 per cent moisture and must be dried before being used. This is done in large hot-air driers, such as are used for drying reclaimed rubber.

After the moisture had been removed from the cotton, it was put through a shredder to remove any small knots and balls of fibers which had formed.

Originally, the extractors were lined with a coarse cloth, which was rather tightly woven. No difficulties were encountered during the first run, but during the second run it was impossible to drain the cement in a reasonable length of time. Apparently, a thin film of rubber had cured on the inside of the cloth during the steaming process. The extractors were then lined with 8-ounce burlap. Much better results were obtained, and therefore on the next run the extractors were relined with 16-mesh galvanized screen, similar to

window screening. The cotton came through this screen, contaminating the cement, and so a 30-mesh steel screen was substituted. This soon rusted and was replaced with one of monel metal. So far these screens have performed very satisfactorily.

When the extraction plant was first put into operation the length of time for steaming varied from 3 to 6 hours. This was an excessive length of time for the evaporation of 300 gallons (1134 liters) of benzene. By the use of hot washes and wire screen lining instead of cloth, the average time of steaming was cut to about 60 minutes.

Applications of Products

The two products obtained during the extraction process from uncured tire ply scrap are cotton, containing about 0.5 per cent rubber, and a 6 per cent rubber cement in benzene. From 1000 pounds (454 kg.) of scrap were obtained 1200 gallons (4536 liters) of cement and about 400 pounds (181 kg.) of cotton.

The first problem was to dispose of the rubber cement. A rubber cement of about the same composition as the cement obtained from the tire ply scrap, but with a higher rubber content, is used in the impregnation of fabric. The problem resolved itself into producing a heavier cement from the 6 per cent extracted cement. The original process called for a still, or evaporator, which would concentrate the cement to the required rubber content. However, this idea was abandoned when it was realized that in evaporating the rubber cement the thin film of rubber next to the heating surface would be cured, and also the low conductivity of the rubber cement itself would make evaporation very difficult. The concentration of the cement was therefore increased by adding fresh stock in the cement mixer.

Aside from a small application in rubber compounding, the cotton may be utilized in paper manufacture and as a filler in cheap felt compositions. It may also be finely ground and used as cotton floc, since the 1 per cent rubber it contains is not detrimental.

Economics of Process

The actual cost of recovering the rubber and cotton by the extraction process is only 30 per cent of the cost of acid reclaiming. In addition the cotton is saved and can be sold, thus increasing the savings effected.

The cotton and rubber are both completely reclaimed without suffering any deterioration. In the other methods for reclaiming uncured ply scrap, either a depreciated product results (acid process) or an incomplete separation of the rubber and cotton may occur (washing process). The power consumption and the labor cost of extracting with solvent are both low.

Limitations of Process

There are several limitations to the extraction process, however. Scraps containing appreciable amounts of reclaim are unsuitable, because cement made from them cannot be used for fabric impregnation. Another difficulty is that it is not practical to mix scraps containing different accelerators, owing to the rapid set-up of the cement under the combined effect of certain accelerators. The process must therefore be operated on one kind of scrap at a time. In order economically to dispose of the cement produced, the extraction of the uncured scrap must operate in conjunction with fabric impregnation. In plants which do not do this the process would have limited applicability.

Acknowledgment

Acknowledgment is made to N. A. Shepard, who initiated the process, and to F. W. Stavely and R. R. Jones, who, with the writer, developed it.

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Graphical Tensile-Testing Machine for Rubber Threads¹

S. H. Hahn and E. O. Dieterich

B. F. GOODRICH CO., AKRON, OHIO

AMONG the many types of physical testing equipment which have been designed for or applied to the needs of the rubber industry, there has never appeared an entirely satisfactory graphical machine for performing tensile tests on small rubber samples, such as the threads and tapes used in making golf balls and elastic fabrics and cords. None of the common machines can be applied directly to the testing of single threads, and even tests on pieces of dumb-bell shape are quite unsatisfactory, largely because the standard machines are comparatively insensitive at low elongations and tensions and also because they depend on the personal accuracy of an operator to observe several points along the stress-strain curve. The Schopper ring test is not entirely successful for tests on threads.

Accordingly it appeared that such tests on light rubber threads could best be made on a curve-drawing machine, designed and constructed especially for the purpose. In many cases, the use of any other machine would have been impossible because frequent tests had to be run on single, cut threads from factory production and on samples taken from storage or from woven fabric.

General Design Requirements

Several rather severe restrictions on the design were imposed by the nature of the samples to be tested. These are as follows:

- (1) The breaking strength of the smallest threads to be tested is comparatively low. A 50×50 gage thread, the smallest

¹ Received September 20, 1930. Presented before the Division of Rubber Chemistry at the 80th Meeting of the American Chemical Society, Cincinnati, Ohio, September 8 to 12, 1930.

ordinarily cut, has a cross-sectional area of only 0.00258 sq. cm. (0.0004 sq. in.) and a breaking strength of less than 450 grams (1 pound). At the same time the heavier threads require a maximum tensile force of about 2 kg. (4 pounds), so that a full scale range of 2.26 kg. (5 pounds) has to be provided.

- (2) Elongations up to about 1000 per cent on a 5.08-cm. (2-inch) gage length have to be accommodated in testing pure gum stocks.
- (3) A high degree of sensitivity as compared with the usual machine is required in the region of 200 to 700 per cent elongation where the tension usually varies from about 40 to 700 grams (0.1 to 1.5 pounds).
- (4) Whatever the grips used, they must not allow the length under test to increase by creep or slippage of the rubber, and they must secure the thread so the gage marks are in full view.

It was found possible to achieve the result desired by modifying a small 11.32-kg. (25-pound) Scott machine designed for graphical stress-strain tests on tire cords. Friction was reduced to a minimum by the use of rotating bearings of small diameter instead of sliding parts, by the elimination of the thread-pulley-counterweight arrangement on the pen motion, by substituting wires for the usual roller chain supporting the upper pulling head of the machine, by using a lighter pen pressure, and by the elimination of the usual ratchet for catching the balance wheel at the breaking point of the sample. The full scale capacity of the machine was reduced to 2.26 kg. (5 pounds) with provision for doubling the range without change of intermediate scale divisions. At the same time, the chart length was not changed materially because a reducing motion provided a chart traverse only one-third that of the lower pulling head.

Tests and almost daily use during the past eighteen months have shown the machine to be entirely satisfactory. Even with the pen in contact with a stationary chart the machine is sensitive to a change of force at the upper head of less than 2 grams (0.005 pound) at any part of its range, a sensitivity better than 0.1 per cent of the full range. The accuracy of a such a machine depends primarily on the care with which the master chart is made and on the accuracy of the printed charts. Checks made on the machine now in use in the writers' laboratories, after several changes of range and recalibrations, showed the indications on the chart to be accurate to about 5 grams (0.01 pound) over the range 0 to 2 kg. (0 to 4 pounds).

Details of Design and Construction

The first problem of the new design shown in Figure 1 was the development of a satisfactory grip, since no amount of work on other parts of the machine would be of much use if the grips allowed the sample to creep or slip. No design was found entirely satisfactory, but it was found possible to secure the ends of the thread sample at the gage marks by use of a simple knot whereby the thread was snubbed

under nearly its maximum elongation around a rod of small diameter. This idea was applied in the form of notched tee of cold-rolled steel, 0.159 cm. ($1/16$ inch) in diameter (see detail of Figure 1), to which the operator secures the thread by stretching it for a short distance on either side of the gage mark, wrapping it around the rod with the mark over the center of the rod in the horizontal plane, crossing one or more times over the first turn immediately above the gage mark, and slipping the free end in the notch at one end of the tee. The appearance of the thread in place on the grip is shown in detail in

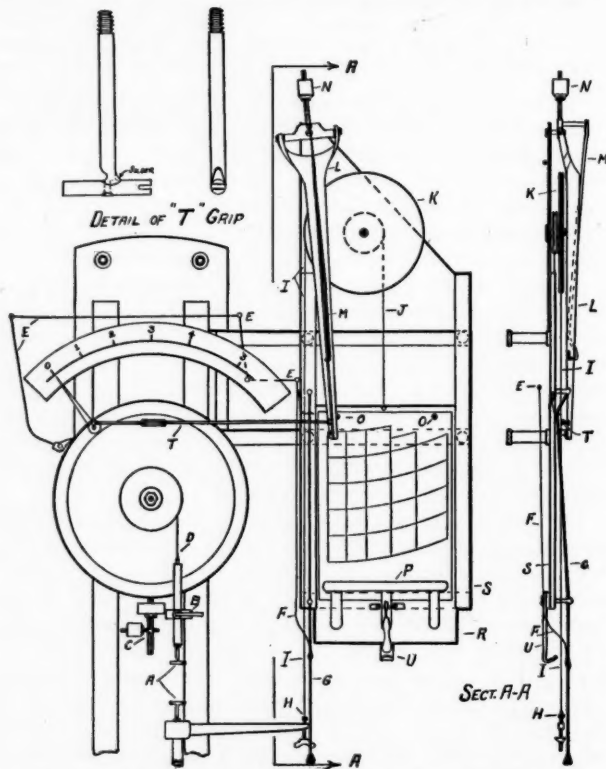


Figure 1—Graphical Rubber-Thread Tester, a Modified Scott Tensile Machine

Figure 2. The upper grip is held in a spring vise, *B*, while fastening the thread. The machine is arranged to return the lower head automatically to a position such that the center-to-center distance between grips is exactly 2 inches (5.08 cm.), the gage length used.

It was hoped that this new grip design would make possible testing up to the true breaking point of the rubber, but subsequent use has shown that most samples break at one grip or the other. A break at one of the grips always occurs

at a lower stress than the maximum breaking strength of the sample, because such breaks are caused by minute chafe marks due to slight creeping of the rubber over the grip as the sample approaches its breaking elongation. The duplication of results, the shape and slope of the stress-strain curve up to about 700 per cent of elongation, and the stiffness or tensile force at a given elongation were, after all, more important than the ultimate breaking strength and elongation in the investigation for which this machine was required.

The pen is carried by a long arm of light-weight construction, *L*, which is counter-balanced by the weight, *N*, and operated by the light rigid metal link, *T*. The pen arm is hinged on an axis perpendicular to its pivot shaft so that the pen may be raised from the paper between tests. A wire of spring steel, *M*, is made a part of the pen-arm construction in such a way that it serves both as a spring to supply a light pen pressure and as a catch to hold the pen

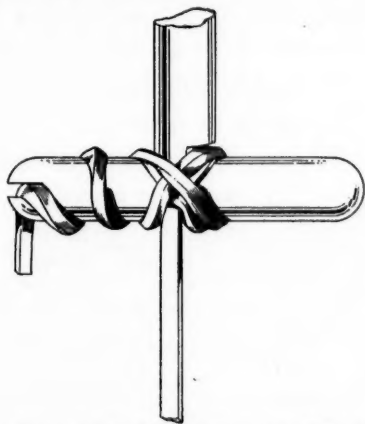


Figure 2—Method of Mounting Thread Test Pieces on Upper Grips

arm in the raised position. The wire is bent to slide in an L-shaped slot near the lower end of the arm. When the arm is raised the end of the wire springs into the short end of the L-slot and holds the arm in that position until it is released by the operator. A vertical, flexible cord is supported behind the pen-arm link in such a way that a light jerk on the cord will move the link forward and raise the pen so that the catch may operate.

The same cord also serves to operate the ratchet device which is used to catch the machine's balance wheel at the instant of rupture of the thread under test. The ratchet spring is so light that the unbalanced weight of the wheel holds the ratchet dog in place until the wheel is advanced slightly, whereupon the wheel may be returned by hand to its zero position. This device was found necessary to prevent the rapid return and violent rebound of the balance

wheel which would otherwise occur after failure of the test sample.

The connecting link, T , was made light enough to have very little effect on the position of the comparatively heavy balance wheel so that the same scale graduations may be used for any tensile range greater than 5 pounds (2.26 kg.).

The chart coördinates are vertical straight lines for the elongation scale, and parallel curves which are concave upwards and slope upwards from left to right for the tensile scale. The vertical scale is made one-third as long as the maximum travel of the lower head of the machine by virtue of the 1:3 reducing-wheel motion by which the motion of

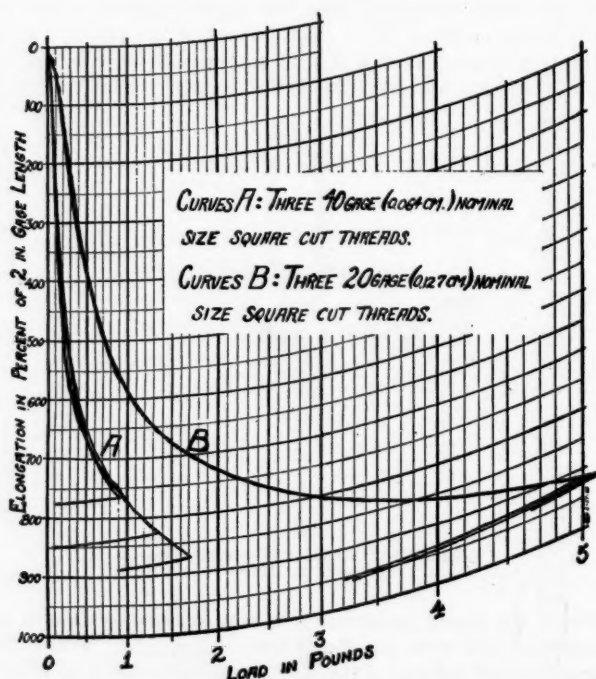


Figure 3—Graph Drawn by Modified Machine

the lower head is transmitted to it. The curved coördinates were laid out from a drawing of a "zero extension" curve to the full tensile capacity of the machine, using a rigid connection between upper and lower heads.

The chart carriage is a rectangular machined plate of 0.318-cm. ($1/8$ -inch) steel supported from the smaller pulley by a fine music wire. A similar wire connects the arm carried by the lower head and the groove in the large pulley. The carriage is guided by accurately machined steel guides supported on a framework bolted to the main frame of the testing machine. A small spring steel clip, U , placed at the

bottom of the guides, prevents the carriage from dropping out in the event of breakage of either wire.

Friction in the force-measuring balance wheel was reduced to a minimum by substitution of a bifilar suspension of fine music wire for the usual small roller chain which was found to be the source of a small variable friction.

The tensile capacity of the machine, although usually fixed at 2.26 kg. (5 pounds), may be increased to 4.52 kg. (10 pounds) or any suitable larger amount by the addition of small weights on the threaded rod, *C*. Calibration is effected by adjustments of both sets of weights, the combination of weights adjustable at right angles to each other in the plane of the wheel with small adjustments of the indicator-needle angle, length of connecting links, and pen radius, being sufficient to bring the device to its original calibration in case of derangement of the original settings.

No change was made in the balance wheel, other than the reduction of the amount of unbalance. A wheel or lever of much lighter construction could readily be substituted for the heavy cast wheel which is standard on the Scott machine, if a reduction of inertia in the measuring system were sought. However, a careful calculation has shown that no serious effects from this source exist when testing threads at the ordinary pulling speeds of 25.4 or 50.8 cm. (10 or 20 inches) a minute.

The extension range of the machine was increased to give a travel of about 50 cm. (20 inches) by lowering the gear box as far as possible. The movement of the upper head of the machine causes the elongation capacity to be less at higher tensiles than it is at zero force.

Operation of Machine

In using the machine the operator locks the upper grip in a position such that the reading on the tensile scale is zero. The printed chart is then secured to the carriage by slipping its perforations over pins, *O*, one of which is adjustable, and fastening it under the clamp bar, *P*. The chart is adjusted so that its vertical coordinates parallel the guide bars and so that its zero force line will coincide with the zero position of the pen. The zero vertical position of the chart is adjusted by use of the adjustable anchor screw, *H*, to which the wire from the lower head of the machine is fastened.

With the upper head still clamped, the operator fastens the previously marked gage length of thread to the two grips. In installing the sample the operator stretches a small portion of the sample near the gage mark to somewhat less than the breaking elongation of the rubber as judged by the feel, lays the gage mark so that it will be horizontally over the center of the cross rod of the tee, and wraps it around the rod and upon itself in a figure eight fashion for four or more turns, always being careful that the turns cross each other slightly above the lower edge of the gage mark so as to leave

the center of the gage mark in full view. The loose end of the thread is secured in the narrow slot at the end. Since the machine is arranged to stop the lower grip in the correct starting position, the installation of the correct gage length over the centers of the grips assures starting the test with zero tensile force on the rubber. The clamp is released by pulling the movable jaw outward and turning it through 90 degrees. The pen is then lowered to the paper by pressing the end of the spring wire out of the short end of the L-slot in the pen arm.

The lower head is then set in motion in the usual way and the stress-strain curve is drawn automatically. At break, a jerk on the cord, *G*, releases the pen from the paper and catches the balance wheel near its maximum deflection. The

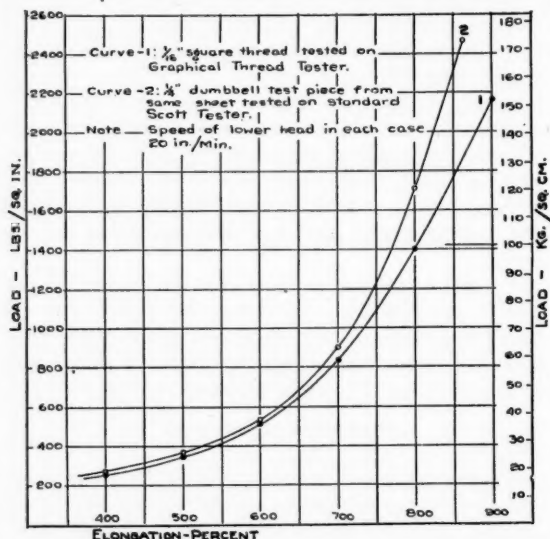


Figure 4—Comparison of Tests on Standard Dumb-Bell-Shaped and Square-Cut Thread Samples

wheel may then be returned under control to its zero position by the operator.

Illustrations of the performance of the modified machine are given in Figure 3, which is a photograph of a graph drawn by the machine. These curves demonstrate that slippage at the grips has been entirely overcome, otherwise there would be a larger spread between the individual curves for the test pieces from a given sample. Of course, variations in the cross section of the test pieces will prevent coincidence of the separate stress-strain curves, but when the proper corrections have been made, the calculated points show close agreement.

Figure 4 is a comparison of the curves obtained for single threads using this machine, and for dumb-bell-shaped test pieces cut from the same sheet and tested in the regular

fashion with the Scott rubber tester. On account of the great differences in geometrical configuration of the two types of test pieces and in the rate of loading, it is to be expected that there will be appreciable differences in the stress-strain curves, such as are indicated here in the region of higher elongations.